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A MANUAL

OF

INORGANIC CHEMISTRY.

VOL. II.

THE METALS.

BY

T. E. THORPE, Ph. D., F.R.S.,

PROFESSOR OF CHEMISTRY IN THE YORKSHIRE COLLEGE OF SCIENCE, LEEDS.

NEW EDITION.

WITH COPIOUS INDEX AND EXAMINATION QUESTIONS AND EXERCISES.

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INORGANIC CHEMISTRY.

CHAPTER I.

PRINCIPLES OF CHEMICAL PHILOSOPHY.

1. Constitution of Matter—Atoms and Molecules.—Many properties of substances are best explained on the supposition that matter is composed of aggregates of what are called *atoms*, but whether these atoms have themselves parts is not known. The chemical molecule is a group of such atoms; it stands in the same relation to the chemical atom that the chemical atom may be conceived to stand to the parts of which it may, for aught we know to the contrary, be composed. A molecule is a group of atoms, as a word is a group of letters, and just as the rearrangement of the same letters may form different words, so the rearrangement of the same atoms may make dissimilar molecules. Or to put it in another, and possibly a better way: an atom stands in the same relation to a molecule that a star does to a solar system; the star itself is a complex body, and possibly the atom of the chemist is equally complex; and just as there are differences in the kinds of stars which make up systems, so there are differences in the nature of the atoms which constitute a molecule. The analogy may be carried even further; for exactly as it is supposed that some of our present systems may have resulted from the disintegration of former systems, so when a molecule is broken up, its atoms rearrange themselves and form other and dissimilar molecules. It is believed that there are some sixty-four different kinds of chemical atoms: these are the *elements* of the chemist; whether they are essentially distinct substances, or are modifications of one or more primordial bodies, is a question which still remains to be answered. The molecule of a body—*that is, the smallest quantity of it which can exist by itself*—is usually made up of at least two atoms, and, with one or two exceptions, this is as true of the elements as of compounds. As a rule, the molecule of an element is composed of not more than two atoms, although instances are not wanting, as in the cases of mercury, zinc, and cadmium, in which the molecule appears to contain only one atom.

The physical relations and properties of a body depend upon the mutual distances and rates of motion of its constituent molecules. In the three so-called physical states of matter—the gas, the liquid, and the solid—the freedom of motion and mean rate of translation of the molecules is greatest in the gas and least in the solid. It will be evident from what has already been stated respecting the molecular condition of gases, that we are possessed of a considerable amount of knowledge of their constitution (Vol. I., p. 61). We have reason to believe that equal volumes of the different gases contain the same number of molecules, consequently we know the relative masses of the molecules of each gas, and the phenomena of gaseous diffusion teach us that these masses are equal in one and the same gas. Moreover, we have determined the mean rate of translation of the molecules of the various gases, and we have made a certain amount of progress towards estimating their number in a given volume, and hence their actual mass and dimensions. It has been shown that about two millions of molecules of hydrogen in a row would occupy a millimetre, and that about two hundred million million million of them would weigh a milligram (Clerk Maxwell). Our knowledge of the constitution of liquids and solids is far less advanced; the conditions regulating the movements of their molecules are much more complicated than in the case of gases.

2. Nature and Action of Chemical Affinity.—We have already defined chemical affinity to be that force which brings about an intimate approximation between the molecules of two substances, so as to form a third body possessed of properties essentially differing from those of its originals, and incapable of destruction by mechanical agencies. Chemistry, then, concerns itself with the study of the internal changes in the constitution of molecules. Of the exact nature of this force we know little, but that it is intimately related to and dependent upon the atomic motions of matter is highly probable. We have reason to believe that it is essentially identical with the power which manifests itself sometimes as light and heat, sometimes as electricity and magnetism.

Many of the phenomena described in the foregoing pages serve to illustrate the modes in which this force operates. We observe in the first place that it acts only at inappreciable distances; bodies must apparently be in absolute contact before they unite. Hence the slowness of the action generally observed between solids when mixed together. Certain solid substances, however, seem to combine with great energy: if a few crystals of iodine are placed on a small piece of phosphorus, the phosphorus takes fire, and phosphorus iodide is formed; in this case, however, the combination is initiated by the action of the vapour of iodine on that of the phosphorus, and so much heat is evolved that combination of the whole rapidly follows from the gradually increasing rapidity of the vaporization. If the materials be strongly cooled before being placed in contact, no action results.

The combination of carbon with iron in the manufacture of steel by the cementation process, has been cited as an illustration of the union of two solids; in reality, however, the carbonization of the iron is effected, as will be shown hereafter, by the action of the gaseous oxides of carbon. By continued contact, however, two solid bodies may be made to unite, especially if agitated together; thus, if potassium and sodium be shaken together under naphtha, they combine to form a fluid alloy. Elements which closely approximate in chemical properties manifest very slight affinity for each other, and the compounds which they form by their mutual union are comparatively unstable; this is well illustrated by the combinations formed by the halogens among themselves.

The mutual affinities of substances are often greatly modified by external circumstances. Of this fact, many examples might be given. Thus mercury at a temperature near its boiling point absorbs oxygen from the air, and mercuric oxide is formed; at a slightly higher temperature this compound is decomposed into its elements. Mercury and oxygen, therefore, at a high temperature, either no longer possess mutual affinities, or under the influence of other conditions, resulting from high temperatures, these affinities are dormant.

Ammonia and hydrochloric acid at ordinary temperatures unite to form ammonium chloride; ammonium chloride at a high temperature is decomposed into ammonia and hydrochloric acid, and at a still higher temperature, the ammonia is resolved into nitrogen and hydrogen, and the hydrochloric acid into hydrogen and chlorine.

Ammonium chloride and calcium carbonate heated together, in a solid state, yield calcium chloride and ammonium carbonate, which volatilises; but on mixing solutions of calcium chloride and ammonium carbonate, ammonium chloride and calcium carbonate are produced.

Steam passed through a red-hot gun-barrel is decomposed into oxygen and hydrogen, and triferric tetroxide (Fe_3O_4) is produced; on passing hydrogen over heated triferric tetroxide, water is formed together with metallic iron. The nature of the reaction depends upon the relative proportion of the gases present; a mixture of steam and hydrogen, in certain proportions, appears to have no effect upon a heated mixture of iron and ferroso-ferric oxide (Fe_3O_4). This particular proportion may be obtained by heating iron with a confined volume of steam, or ferroso-ferric oxide with a confined volume of hydrogen; after a time all chemical action appears to cease.

The decomposition of many bodies under the influence of heat is modified in a very remarkable manner by conducting the process in sealed vessels, or under such conditions that the products are not removed from the sphere of action. Phosphorus pentachloride, on heating, is readily and completely decomposed into the trichloride and free chlorine, if heated in an open vessel, or if the chlorine be allowed to escape by diffusion; hence it was formerly supposed that the molecule of phosphorus pentachloride could not exist in the gaseous state. If, however, the pentachloride be heated in a confined space already saturated with the vapour of the trichloride, it is quite possible for it to exist as a gas; and by taking advantage of this fact, Wurtz has succeeded in showing that it possesses the normal vapour density.

On the other hand, by rapidly separating the dissociated molecules, or by lowering their temperature, the rate of decomposition of a substance by heat is greatly augmented. As Grove showed many years ago, steam, at a high temperature, is resolved into oxygen and hydrogen, which recombine in great measure on cooling; if, however, some substance be present capable of removing, even temporarily, one of the gases, recombination will be prevented; thus when steam is passed over melted silver, free hydrogen is obtained, the oxygen being dissolved by the metal as it would be in water or alcohol. Other compound gases, as sulphur dioxide and the oxides of carbon, may be decomposed in like manner if care be taken to lower the temperature of the liberated products below the point at which they recombine.

As we have seen, many compound gases may be decomposed by the continued passage of induction sparks; the action of the spark is entirely due to its high temperature. The molecules in its neighbourhood are alone decomposed, and the products immediately diffuse into the cold mass of the gas, whereby their temperature is reduced below that at which they combine. Obviously, after a time, the reverse action would take place, and the products will commence to recombine; hence there must be a certain mixture of the original gas and decomposed products at which no action will appear to occur.

Ordinary solid paraffin may be volatilised by heat, and at a high temperature may be dissociated into a mixture of hydrocarbons of the C_nH_{2n+2} and C_nH_{2n} series, the greater proportion of which seem to recombine on lowering the temperature; if, however, the dissociated molecules be removed as rapidly as they are formed, the whole of the solid paraffin may be gradually decomposed into a mixture of liquid hydrocarbons. Stearic acid, under similar conditions, is also decomposed into gaseous and liquid products.

Acetic acid added to potassium carbonate expels carbon dioxide and forms potassium acetate; if, however, potassium acetate be dissolved in alcohol, and treated with carbon dioxide, potassium carbonate is reproduced, together with free acetic acid; the carbonate, being insoluble in alcohol, is precipitated as fast as it is produced.

Strong nitric acid heated with lead chromate forms chromic acid and lead nitrate, which is almost insoluble in the strong acid; on the addition of water, the reverse change occurs, lead chromate is reproduced, together with free nitric acid.

A remarkable instance of the effect of extraneous conditions in modifying chemical action is seen in the formation of ethene chloriodide (C_2H_4ICl). This curious substance, the analogue of Dutch liquid, unlike that liquid, cannot be readily formed by the direct union of its components. If ethene and iodine chloride be brought together, ethene dichloride and free iodine are formed:

$$C_2H_4 + 2\,ICl = C_2H_4Cl_2 + I_2$$

In reality, however, the reaction occurs in two phases: the chloriodide is first formed, but under the influence of a second molecule of the iodine chloride it is decomposed with the formation of Dutch liquid and iodine:

$$(1)\quad C_2H_4 + ICl = C_2H_4ICl.$$
$$(2)\quad C_2H_4ICl + ICl = C_2H_4Cl_2 + I_2.$$

By adding iodine chloride to water a portion is decomposed in accordance with the equation:

$$5ICl + 3H_2O = 5HCl + HIO_3 + 2I_2,$$

the extent of the decomposition depending on the ratio of the amount of the products of decomposition to the amount still undecomposed. This is proved by the fact that the liquid after a time experiences no further change, but that if the precipitated iodine be removed, either by filtration or by the addition of carbon bisulphide, a further decomposition ensues. The solution dissolves iodine monochloride in considerable quantity, and if treated with a current of ethene gas, ethene chloriodide separates out immediately, since it is insoluble in water. Its rapid removal by precipitation from the solution containing the monochloride is probably the cause of its permanence under these conditions.

Pressure frequently exercises a very marked effect upon the progress and direction of a chemical change. Thus the decomposition of the paraffin, above cited, is greatly augmented by increasing the pressure under which the reaction occurs.

Acetic acid expels carbon dioxide from marble at the ordinary pressure and temperature; but, under great pressure, a solution of calcium acetate is decomposed by carbon dioxide with formation of crystallised calcium carbonate. Certain reactions can only be produced under the influence of pressure. On the other hand, some reactions, as in the case of the action of acids upon zinc (see Vol. I., p. 51), are completely arrested by great pressure.

The relative proportions of the reacting bodies, or of the products, frequently influence the result of the change. This was clearly pointed out by Berthollet many years ago, but the attempt made by him to include the observed phenomena under certain general laws has been only partially successful. (For further details, the student is referred to *Watts' Dictionary of Chemistry*, Vol. I., and Supplements I. and II., Art. "*Chemical Affinity.*")

3. Relations of Chemical Affinity to Heat.—Every manifestation of chemical action is accompanied by a thermal disturbance, usually consisting in the production of heat. To take a simple case: bromine added to amylene, forms amylene dibromide, and a considerable amount of heat is evolved. Here the heat results entirely from the chemical reaction between the two substances; the reacting bodies are liquids, and the product is a liquid, and no change of volume follows the union. As a rule, the thermal phenomena observed in chemical changes are very complicated, and the effect is frequently the nett result of opposing reactions. Thus a considerable rise of temperature is observed in the preparation of hydrogen from zinc and sulphuric acid, but the actual development of heat is much less than should result from the direct chemical action. The action of the acid upon the metal and the partial hydration of the zinc sulphate generate heat; on the other hand, the solution or liquefaction of the salt, and the liberation of the gas, produce cold; and the phenomena is further complicated by other secondary effects, some operating in one direction and some in the other; hence the result is simply the balance of opposite tendencies.

The actual amount of heat or cold generated in a given chemical change is, however, invariable, and is a physical constant of great importance. Thus 1 gram of hydrogen in combining with oxygen to form water evolves sufficient neat to raise 34,000 grams of water from 0° to 1° C.; in combining with 35·5 grams of chlorine, to form hydrochloric acid, it evolves about 22,000 *units of heat;* that is, sufficient heat to raise 22,000 grams of water from 0° to 1°.

The following Table shows the amount of heat generated by the union of certain elements with oxygen:—

HEAT OF COMBINATION OF ELEMENTS WITH OXYGEN.

	Product.	Weight burned in grams.	Grams of water heated from 0° to 1°.	Observer.
Hydrogen, ...	H_2O (liquid)	1	33,881	Andrews.
,, . . .	,, ,,	1	34,462	Favre and Silbermann
,, ...	,, ,,	1	34,178	Thomsen.
Carbon—				
a. Charcoal, . .	CO_2 (gas)	12	94,800 96,960	Andrews Favre and Silbermann
b. Graphite, . .	CO_2 ,,	12	93,564	
c. Diamond, . .	CO_2 ,,	12	93,240	,,
Phosphorus—				
Yellow, ...	P_2O_5 (solid)	31	184,543	,,
Red, ...	,, ,,	31	157,170	,,
Sulphur—				
a. Octahedral, .	SO_2 (gas)	32	71,040	Favre and Silbermann
b. Prismatic, . .	SO_2 ,,	32	72,320	
Iron, ...	Fe_3O_4	56	88,592	Andrews.
Zinc, ...	ZnO	65·2	86,450	,,
Tin, ...	SnO_2	118·1	135,360	,,
Copper, ...	CuO	63·1	38,304	,,

HEAT OF COMBINATION OF THE HALOGENS WITH HYDROGEN.
(Thomsen.)

	Product.	Weight Burned	Heat Units.
Chlorine, ...	HCl	35·5	22,000
Bromine, ...	HBr	80	8,440
Iodine, ...	HI	126·7	– 6,036

The amount of heat actually produced in these reactions depends upon the physical state of the products. Thus, in the case of the union of oxygen and hydrogen, it is made up of that formed by the actual combination, together with the amount produced by the condensation of the vapour. The quantity of heat evolved also varies with the molecular condition of the reacting body; this is seen in the cases of sulphur and the different allotropes of carbon and phosphorus. A certain amount of heat seems to be utilised in bringing them to a particular molecular condition before combination occurs. In the case of the formation of hydriodic acid, heat is *absorbed.* In all cases the thermal effect is simply the nett result of a series of positive and negative actions; and it may happen that the amount of heat needed to change the state of the iodine, and to effect the disunion of the hydrogen and iodine molecules prior to combination, is greater than is actually evolved in their union; hence heat has to be supplied externally, that is, from the apparatus in which the change occurs, and cold results.

The amount of energy required to undo the work of combination is doubtless equal to that needed in its production; hence the greater the development of heat in the formation of a body, the greater is its stability. This is well seen in the case of the combinations of hydrogen with the halogens; the greatest heat is evolved in the formation of hydrochloric acid, and this body is by far the most stable of the three hydrides. Thomsen has also shown that the amount of heat evolved in the formation of the oxygen compounds of iodine is much greater than that evolved in the production of the corresponding chlorine compounds, and still greater than that yielded by the union of bromine and oxygen; the order of stability observed among the haloid compounds of oxygen agrees precisely with this result. So, too, in the case of the sulphur acids: the most stable member of the series is sulphuric acid, and the largest amount of heat is developed in its formation.

The combination of oxygen with many substances may be supposed to occur in two or more phases: thus, since carbon unites with oxygen in two proportions, it may be assumed that the first phase consists in the formation of the monoxide, and that this gas afterwards combines with a second atom of oxygen to form the dioxide. Experiment has shown that the heat evolved in the union of oxygen with copper and tin, to form the cuprous and stannous oxides, is exactly half ot that generated in converting the metals into cupric and stannic oxides. Carbon apparently forms an exception in this respect, since the amount of heat evolved in the transformation of the monoxide to the dioxide is much greater than that formed in the conversion of carbon to the monoxide; but the difference may be due to heat being absorbed in changing the physical state of the carbon.

On dissolving a salt in water, the usual thermal effect is the production of cold, since heat is absorbed in the liquefaction of the solid; but in certain cases, as in the addition of dehydrated sulphates of copper or zinc to water, a great amount of heat is evolved, due primarily to the chemical union of the water with the salt. The actual amount of heat produced is, however, less than that corresponding to this action, since a certain amount is absorbed in dissolving the product. Many gases dissolve in water with considerable rise of temperature, the heat being due partly to the liquefaction of the gas, and partly to its chemical action on the water.

On mixing many liquids, such as alcohol and water, and sulphuric acid and water, a considerable amount of heat is developed. The quantity of heat evolved in the hydration of sulphuric acid is seen in the following Table; the numbers in the second and third columns express the amount in kilogram degrees evolved in the formation of the several hydrates from 1 gram H_2SO_4, as observed by Favre and Quaillard, and by Pfaundler.

		Favre and Quaillard.	Pfaundler.
H_2SO_4 with	H_2O	66·4	69·72
,, ,,	$2H_2O$	99·5	103·44
,, ,,	$3H_2O$	118·3	118·85
,, ,,	$4H_2O$	130·1	131·73
,, ,,	$5H_2O$	139·2	140·80
,, ,,	$6H_2O$	146·9	148·09
,, ,,	$120H_2O$	..	181·16

4. Laws of Combination by Volume—Specific Volume.— 1. *Of Gases.*—Since equal volumes of two gases, measured under like conditions, contain as a rule the same number of molecules, it follows that the volumes of any two gases, which unite to form a third gas, must be to one another in the same ratio as the number of molecules combining to form the third molecule. Thus one molecule of hydrogen unites with one molecule of chlorine to form two molecules of hydrochloric acid gas; hence since a given volume of hydrogen and of chlorine contains the same number of molecules, it is evident that hydrogen and chlorine must combine in equal volumes to form hydrochloric acid gas. In like manner, to form the molecule of water (H_2O), two volumes of hydrogen unite with one volume of oxygen; so, too, in the case of ammonia (NH_3), nitrogen and hydrogen unite in the proportion of one volume of the former to three of the latter. What is true of the simple gases is equally true of the compound gases; we find that the combination of compound gases with simple gases, or of compound gases with one another, is regulated by laws as simple as those which determine the combination of the elementary gases alone. These laws were first stated by Gay-Lussac; he found that the volumes in which gases combine can be expressed by such simple numbers as those above given; and that the volume of the compound gas always stands in a very simple relation to the sum of the volumes of its constituents before combination.

We have already seen that the molecule of a compound gas occupies the same volume as the molecule of hydrogen, or twice the volume occupied by the atom of hydrogen; accordingly, the specific gravity of a compound gas is half its molecular weight, hydrogen being the unit (Vol. I., p. 157). The number obtained by dividing the molecular weight of a body by its specific gravity is termed its *specific volume;* in the case of gases, both simple and compound, this number is equal to 2.

2. *Of Liquids and Solids.*—Comparatively little is known of the laws of combination by volume of liquid and solid bodies, and what has actually been observed does not admit of such simple expression, and is by no means so generally applicable, as in the case of gases.

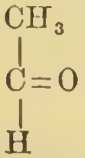
In comparing the specific volumes of liquids, it is necessary to know their specific gravities under comparable conditions of temperature, as at the points at which their vapour tensions are equal, *e.g.*, at their boiling points. Kopp, by whom the relations between the specific volumes of liquids have been chiefly investigated, has shown—

1. That many isomeric liquids have identical specific volumes. Thus acetic acid and methyl formate ($C_2H_4O_2$), and butyric acid and ethyl acetate ($C_4H_8O_2$), have respectively the same specific volume.

2. In a series of bodies a difference of nCH_2 is equal to $n22$. Thus ethyl acetate differs from methyl butyrate by CH_2; the difference in their specific volumes is 22. Methyl formate and ethyl butyrate differ by $4CH_2$, the difference in their specific volumes is 4 × 22.

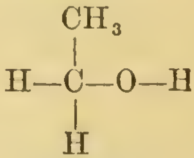
3. It is found that an atom of carbon can replace two atoms of hydrogen in a compound without alteration of specific volume. Accordingly, it follows since the specific volume of the group CH_2 is 22, that the specific volume of C is 11, and that of H is 5·5. The specific gravity of water at the boiling point is 0·9579 (Kopp), hence its specific volume $= \frac{18}{0{\cdot}9579} = 18{\cdot}8$; and since the specific volume of $H_2 = 5{\cdot}5 \times 2$, the specific volume of O is $18{\cdot}8 - 11{\cdot}0 = 7{\cdot}8$. As a rule, the specific volume of an element is invariable when in combination; thus, carbon has invariably the specific volume 11; hydrogen that of 5·5; chlorine that of 22·8. But this law does not hold good in the case of oxygen; the specific volume of this element is found to vary with the manner in which it is held in union. When its affinities are divided between two atoms, as in water, it has the volume 7·8; when it is combined with only one atom its specific volume becomes 12·2. Sulphur also forms an exception; when united to one atom its specific volume is 28·6, but when attached to two atoms its specific volume is 22·6.

Thus in the cases of aldehyd and alcohol—



$$\begin{array}{c} CH_3 \\ | \\ C=O \\ | \\ H \end{array}$$

Aldehyd.
Spec. vol. of O = 12·2.



$$\begin{array}{c} CH_3 \\ | \\ H—C—O—H \\ | \\ H \end{array}$$

Alcohol.
Spec. vol. of O = 7·8.

From the fact that the specific volumes of the elements are as a rule invariable, it becomes possible to calculate the specific volumes, and hence the specific gravities, of many liquid bodies. Moreover, the knowledge of the specific volume of a compound may be employed, as will be shown hereafter, to determine the chemical value of an element.

It appears that the members of certain groups of analogous elements possess a common specific volume when in the solid state; this seems to be true of selenium and sulphur, molybdenum and tungsten, cobalt and nickel, iron and manganese, and of the members of certain other groups. It is not, however, true of analogous elements when in combination in liquids, even in similarly-constituted compounds. Thus, in the case of the following groups of compounds, it is seen that the specific volume increases with the molecular weight of the element—

	Mol. wt.	Spec. vol.
PCl_3	137·38	93·54
$AsCl_3$	181·53	94·64
$SbCl_3$	228·68	97·82
$SiCl_4$	169·94	121·13
$TiCl_4$	191·84	126·03
$SnCl_4$	259·94	131·41
$POCl_3$. . . .	153·38	101·58
$VOCl_3$ . . .	173·73	106·54

The molecular weight of bromine is nearly equal to the mean of the molecular weights of its analogues, chlorine and iodine; hence the molecular weights of bromine and iodine monochloride (ICl) are nearly equal. These bodies are liquids, and greatly resemble each other in physical properties. But their specific volumes are not equal: that of bromine is 53·62, whilst that of iodine chloride is 56·32, and the difference is preserved in the correlated derivatives, ethene dibromide and ethene chloriodide. By subtracting the specific volume of C_2H_4, calculated by means of the values already given for C and H, from the specific volume of the ethene bromide and chloride, we obtain numbers which are almost identical with those found directly for bromine and iodine chloride. We are thus warranted in concluding that bromine and iodine chloride possess the same volume in a compound which they have in the free state. It has also been shown that this is true of many solid bodies, particularly of the heavy metals, but that it is not true of the lighter metals, as of the alkalies. Hence it follows that, as a rule, *equivalent quantities of various elements, in uniting with the same quantity of a given element, receive equal increments of volume* (Schröder; Kopp). If, therefore, we determine the specific volumes of a number of metals, and of their oxides or chlorides, the differences between the two sets of values afford us the means of calculating the specific volumes of oxygen and of chlorine when in combination in a solid body. The numbers thus obtained for oxygen and chlorine are less than those calculated from liquid compounds. This, indeed, is what we should expect; for the specific volume of a body is the space occupied by its atoms, together with the interstitial spaces, and we have reason to believe that these interstitial spaces are less in solid than in liquid bodies. The densities of many isomorphous bodies are proportional to their molecular weights, hence it follows that many isomorphous compounds have equal specific volumes. Thus in the case of the isomorphous sulphates of magnesium and zinc—

	mol. wt.	sp. gr.	spec. vol.
$MgSO_4.7H_2O$ - - -	246·07	1·678	146·7
$ZnSO_4.7H_2O$ - - -	287·23	1·963	146·2

Thus, too, in the case of the carbonates of lead and strontium—

	mol. wt.	sp. gr.	spec. vol.
$SrCO_3$ - - - -	147·54	3·605	40·92
$PbCO_3$ - - - -	266·9	6·47	41·26

These two compounds, moreover, possess the same molecular heat; hence it would appear that Avogadro's law may, in a limited sense, be extended to solid substances; we may say that equal volumes of certain solid bodies contain the same number of molecules.

It has been shown that in all cases where a transposition takes place between solids, the products being solids, the sum of the specific volumes of the reacting bodies is always greater than the specific volumes of the products; in other words, the transposition is always accompanied by contraction. It would further seem that the energy of the reaction and the stability of the resultant products depend upon the amount of contraction which occurs.

It has been pointed out that the volume of certain highly-hydrated salts, as the phosphates and arsenates of sodium, which crystallise with twelve molecules of water, and sodium carbonate, which ordinarily crystallises with ten molecules, is exactly equal to the volume of the water they contain considered as ice. It would seem that in these salts the atoms of the acid and base must exist in the interstitial spaces since they do not increase the bulk (Playfair and Joule). On the other hand, in the cases of certain other classes of salts, as the alums and the sulphates of the form $M''SO_4, 6H_2O$, the volume appears to be made up of that of the solid water and that of the metallic oxide.

5. Quantivalence of the Elements.—On comparing the composition of the hydrides of the non-metallic elements, it becomes evident that these elements differ greatly in their power of combining with hydrogen; and that, indeed, they may be classed into comparatively few groups, in accordance with this property. For instance, each member of the group of the halogens combines with only *one* atom of hydrogen—

HF, Hydrogen fluoride.
HCl, Hydrogen chloride.
HBr, Hydrogen bromide.
HI, Hydrogen iodide.

Each of the members of the sulphur group has the power of uniting with *two* atoms of hydrogen—

H_2O, Water.
H_2S, Hydrogen sulphide.
H_2Se, Hydrogen selenide.
H_2Te, Hydrogen telluride.

Each member of the nitrogen group can hold in stable union *three* atoms of hydrogen—

H_3N, Hydrogen nitride.
H_3P, Hydrogen phosphide.
H_3As, Hydrogen arsenide.
H_3Sb, Hydrogen antimonide.

Lastly, an atom of carbon and of silicon can combine with *four* atoms of hydrogen—

H_4C, Methane.
H_4Si, Hydrogen silicide.

Chlorine may be made to replace the hydrogen in methane atom after atom; we thus get the following series:—

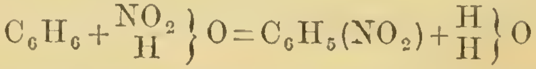
$$CH_4,\ CH_3Cl,\ CH_2Cl_2,\ CHCl_3,\ CCl_4.$$

It is evident from these formulæ that chlorine is chemically equivalent to hydrogen; we have also seen that for each hydride of the sulphur group and of the nitrogen group, we have a corresponding chloride. We may therefore, if we please, make chlorine our standard of the chemical value, or atom-fixing power of the elements.

It appears, therefore, that the various non-metallic elements have different combining capacities or affinity-values, as measured by their power of holding in stable union atoms of hydrogen or chlorine, or other substance chemically equivalent to these; this is expressed by saying that their *quantivalence* is different.

Now what is true of the non-metals in this respect is equally true of the metals; this, indeed, we should expect, for we have no *á priori* reason for believing that the two groups would show a radical difference in this particular when we fail to perceive it in any other. We may therefore classify the elements into groups, depending upon their chemical values or quantivalence.

And not only may the elements be so classed, but also those groups of elements or compound radicles, as they are termed, which, as in the case of cyanogen, go in and out of combination like a simple body. The parallelism which exists between the combinations of chlorine and cyanogen has already been exhibited; it is evident that this compound radicle is chemically equivalent to chlorine. When benzene is acted upon by nitric acid, nitrobenzene is formed—



$$C_6H_6 + \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = C_6H_5(NO_2) + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

the radicle NO_2 has replaced an atom of hydrogen in the benzene, it is evidently, therefore, chemically equivalent to hydrogen, and, like that element, has the power of uniting with an atom of chlorine; it thus forms *nitryl chloride* (NO_2Cl).

When sulphur dioxide is brought into contact with chlorine, *sulphuryl chloride* (SO_2Cl_2) is formed; a similar compound with bromine is known. Moreover, a moiety of the chlorine may be replaced by the group NO_2 or OH; or both atoms of the chlorine may be replaced by the latter group; thus

$$SO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. \qquad SO_2\left\{\begin{matrix}Br\\Br\end{matrix}\right. \qquad SO_2\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$$

Sulphuryl chloride. Sulphuryl bromide. Sulphuryl hydroxyl chloride.

$$SO_2\left\{\begin{matrix}NO_2\\Cl\end{matrix}\right. \qquad SO_2\left\{\begin{matrix}NO_2\\OH\end{matrix}\right. \qquad SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

Sulphuryl nitryl chloride. Leaden chamber crystals. Sulphuric acid.

It is evident from the above formulæ that this group SO_2 has the power of combining with two atoms of chlorine, or with the chemically equivalent quantity of any other element or compound radicle.

The groups *phosphoryl* (PO) and *phosphothionyl* (PS) can combine with three atoms of chlorine, or an equivalent amount of any other element or compound radicle; thus

$$PO\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. \qquad PO\left\{\begin{matrix}HO\\HO\\HO\end{matrix}\right. \qquad PS\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.$$

Phosphoryl chloride. Phosphoric acid. Phosphothio-chloride.

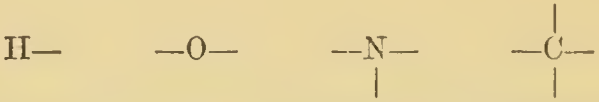
Elements or compound radicles which have the power of uniting with only one atom of hydrogen or chlorine, or of any other element chemically equivalent to these, are termed *monads*, or are said to be *monovalent.* When they unite with two atoms they are *dyads* or *divalent;* when with three atoms they are *triads*, or are *trivalent;* with four atoms, *tetrads;* with five atoms, *pentads;* with six atoms, *hexads.*

The chemical value of the element or compound radicle may be indicated by placing the corresponding Roman numeral over the symbol, thus:

$$\overset{\text{I}}{CN} : \overset{\text{II}}{O} : \overset{\text{II}}{SO_2} : \overset{\text{III}}{N} : \overset{\text{III}}{PO} : \overset{\text{IV}}{C}.$$

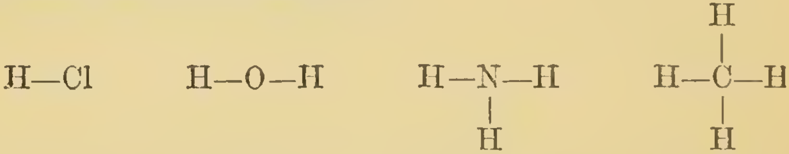
Comparatively few of the metals unite with hydrogen, but all of them combine with chlorine, which is chemically equivalent to hydrogen; hence the quantivalence of the elements is most frequently deduced from their combinations with chlorine.

In order to exhibit the mode in which the combining powers are satisfied in a compound, it is usual to attach to the symbols of the elements or compound radicles a number of strokes equal to the number of units of affinity which they possess; thus:



$$\mathrm{H}-\qquad -\mathrm{O}-\qquad -\underset{|}{\mathrm{N}}-\qquad -\overset{|}{\underset{|}{\mathrm{C}}}-$$

We may thus represent the composition of hydrochloric acid, water, ammonia, and methane:



$$\mathrm{H}-\mathrm{Cl}\qquad \mathrm{H}-\mathrm{O}-\mathrm{H}\qquad \mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H}\qquad \mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H}$$

and since an atom of oxygen is chemically equivalent to two atoms of hydrogen, it is capable of neutralising two combining units of an element or compound radicle, thus:

$\overset{II}{S}O_2=O$
Sulphur trioxide.

$O=C=O$
Carbon dioxide.

A dyad like oxygen or sulphur may, however, unite with an element or group of elements with only one of its affinities, the other remaining free or capable of saturation by union with a second atom of a dyad; thus in the case of the potassium sulphides:

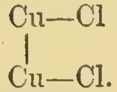
Monosulphide, - - K—S—K
Disulphide, - - - K—S—S—K
Trisulphide, - - K—S—S—S—K
Tetrasulphide, - - K—S—S—S—S—K.

It is evident, therefore, that the atomic value of a body cannot be unequivocally deduced from its combinations with divalent elements.

The quantivalence of an element is, however, not always immediately indicated by the composition of its haloid derivatives, since it frequently happens that the body has the power of uniting with chlorine and its congeners in more than one proportion; thus we have two compounds of copper and chlorine, one of which contains twice as much chlorine as the other. The simplest expression of the analysis of these compounds would be respectively

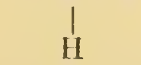
$CuCl$ and $CuCl_2$;

the first formula would seem to indicate that Cu is a monad, the second that it is a dyad. Other considerations, however, lead to the belief that copper is divalent; hence we suppose that a molecule of the lower chloride contains two atoms of copper combined with two atoms of chlorine, thus—

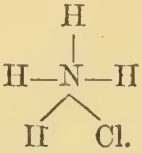


$$\begin{array}{l} \text{Cu—Cl} \\ \ | \\ \text{Cu—Cl.} \end{array}$$

But there are a number of cases in which a body combines in different proportions with a monad which cannot be so explained, since the number of atoms in the molecule admits of direct determination; thus phosphorus and tin each form two chlorides, $SnCl_2$ and $SnCl_4$, PCl_3 and PCl_5. In the trichloride, phosphorus would seem to be a triad, and in the pentachloride, a pentad; that is, phosphorus possesses a variable atomic value; so, too, with tin: in the dichloride it is a dyad, and in the tetrachloride it is a tetrad. It will be evident from the examples of the chlorides of copper that the atomic value of an element can only be deduced with certainty when we know the number of atoms present in the molecules of its haloid compounds. The most generally applicable mode of determining the molecular weight of a body is from its vapour density. But it happens that the vapour density of many of these compounds which seem to afford a variable atomic value for an element cannot be determined, for the reason that the body is not volatile, or if volatile, is readily dissociated. Thus the nitrogen in ammonia appears to be triadic, but in the combination of ammonia with hydrochloric acid, sal-ammoniac, this element would appear to be a pentad—



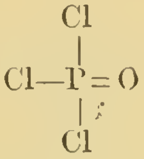
$$\begin{array}{c} \text{H—N—H} \\ | \\ \text{H} \end{array}$$



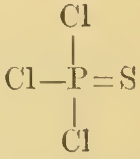
$$\begin{array}{c} \text{H} \\ | \\ \text{H—N—H} \\ \diagup\ \diagdown \\ \text{H}\quad\text{Cl.} \end{array}$$

But when ammonium chloride is volatilised, it is decomposed into ammonia and hydrochloric acid.

It has been shown that phosphorus pentachloride can exist in the gaseous state between certain narrow limits of temperature and pressure, but the combination is easily decomposed into the trichloride and free chlorine. Two chlorides of iodine are known; a monochloride ICl, and a trichloride ICl_3; accordingly, iodine may be regarded as a monad or as a triad. But the trichloride cannot be volatilised; on heating, it is dissociated into the monochloride and free chlorine. Hence these combinations NH_4Cl, PCl_5, and ICl_3 have been regarded as of little value in demonstrating the higher quantivalence of N, P, and I, respectively. Ammonium chloride may be considered as a combination of the molecule NH_3 with the molecule HCl; phosphorus pentachloride of a molecule of the trichloride and a molecule of chlorine; iodine trichloride of a molecule of the monochloride and a molecule of chlorine. The chlorine is supposed to be combined with the phosphorus trichloride and the iodine chloride in a manner similar to that in which it is combined with water in the chlorine hydrate ($Cl_2.10H_2O$), or in the mode in which HCl is united to $PtCl_4$ in the compound $2HCl.PtCl_4$. In the case of ammonium chloride, the ammonia may be supposed to be united to the hydrochloric acid in the same manner that it is united with silver chloride in the compound $AgCl.3NH_3$. Phosphoryl chloride ($POCl_3$) and phosphoryl thiochloride ($PSCl_3$) are regarded as indicating the pentadicity of phosphorus, and they have been thus formulated:

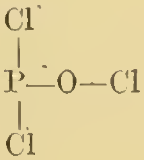


$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}P{=}O}\\ |\\ \mathrm{Cl}\end{array}$$

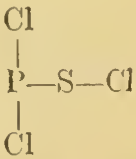


$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}P{=}S}\\ |\\ \mathrm{Cl}\end{array}$$

But if phosphorus be a triad these compounds must be thus represented:



$$\begin{array}{l}\mathrm{Cl}\\ |\\ \mathrm{P{-}O{-}Cl}\\ |\\ \mathrm{Cl}\end{array}$$



$$\begin{array}{l}\mathrm{Cl}\\ |\\ \mathrm{P{-}S{-}Cl}\\ |\\ \mathrm{Cl}\end{array}$$

The difference between the two formulæ is that in the one case the oxygen and the sulphur are united to the phosphorus by both their affinities, whereas, in the second case, they are united by only one affinity, the other being combined with chlorine. We have already stated that the specific volumes of oxygen and of sulphur vary with the manner in which these bodies are held in union. When attached to two atoms, oxygen has a specific volume 7·8, and sulphur that of 22·6; but when both affinities are satisfied by combination with a single atom, oxygen and sulphur have respectively the specific volumes 12·2 and 28·6. Accordingly, if phosphorus be a pentad in $POCl_3$ and $PSCl_3$, the specific volume of O and S must be respectively 12·2 and 28·6; if, however, it is a triad, the values must be 7·8 and 22·6. Experiment shows that the specific volume of PCl_3 is 93·68, that of $POCl_3$ is 101·57, and that of $PSCl_3$ is 116·34.

$$\begin{array}{ccccc} POCl_3 & - & PCl_3 & = & O \\ 101{\cdot}57 & - & 93{\cdot}68 & = & 7{\cdot}89 \\ PSCl_3 & - & PCl_3 & = & S \\ 116{\cdot}34 & - & 93{\cdot}68 & = & 22{\cdot}66 \end{array}$$

Hence it would appear that phosphorus is a triad in these compounds.

The existence of a perfectly stable pentafluoride (PF_5), which is gaseous under ordinary conditions, nevertheless proves that phosphorus may be a pentad in certain combinations. Accordingly, we must conclude that this element possesses a variable atomic value, depending upon the conditions under which its affinities exert themselves. The consideration of many similar cases leads us to conclude that we cannot affix an absolute atomic value to any element.

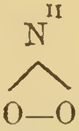
As a general rule, the variation in atomic value of the same element follows a very simple law; the quantivalence varies by two units. Thus phosphorus is triad and pentad; tin is a dyad and a tetrad; sulphur is a dyad, a tetrad, or a hexad; we never find that phosphorus is a dyad or tetrad, or that sulphur and tin are triads and pentads.

The elements have accordingly been divided into two great classes: (1) of *perissads*, or elements of odd atomic value; and (2) of *artiads*, or elements of even atomic value.

Still it would seem probable that an element may sometimes behave as an artiad, and at other times as a perissad. Thus nitrogen has usually an odd atomic value, but in the dioxide at ordinary temperatures, and in the tetroxide above 140° it would seem to be an artiad·

$$\overset{\mathrm{II}}{\mathrm{N}}=\mathrm{O}$$

Nitrogen dioxide.



or $\mathrm{O}=\overset{\mathrm{IV}}{\mathrm{N}}=\mathrm{O}$

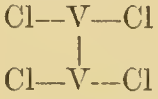
Nitrogen tetroxide.

Vanadium is usually a perissad, but in the dichloride and tetrachloride, and in the vanadyl dichloride and dibromide, it must be regarded as an artiad if the simplest results of the analysis of these compounds be considered to express the composition of their molecules:

$$\overset{\mathrm{II}}{\mathrm{V}}=\mathrm{Cl}_2 \qquad \mathrm{Cl}_2=\overset{\mathrm{II}}{\mathrm{V}}=\mathrm{Cl}_2 \qquad \mathrm{Cl}_2=\overset{\mathrm{II}}{\mathrm{V}}=\mathrm{O} \text{ or } \mathrm{Cl}-\overset{\mathrm{II}}{\mathrm{V}}-\mathrm{O}-\mathrm{Cl}.$$

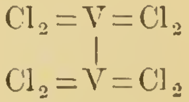
Vanadium dichloride. Vanadium tetrachloride. Vanadyl dichloride.

The odd atomic value, however, is preserved if these formulæ be doubled:



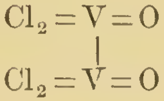
$$\begin{array}{c}\mathrm{Cl{-}V{-}Cl}\\ |\\ \mathrm{Cl{-}V{-}Cl}\end{array}$$

V_2Cl_4



$$\begin{array}{c}\mathrm{Cl_2{=}V{=}Cl_2}\\ |\\ \mathrm{Cl_2{=}V{=}Cl_2}\end{array}$$

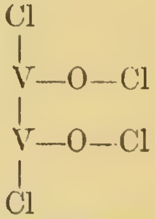
V_2Cl_8.



$$\begin{array}{c}\mathrm{Cl_2{=}V{=}O}\\ |\\ \mathrm{Cl_2{=}V{=}O}\end{array}$$

$V_2O_2Cl_4$;

or,

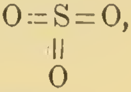


$$\begin{array}{l}\mathrm{Cl}\\ |\\ \mathrm{V{-}O{-}Cl}\\ |\\ \mathrm{V{-}O{-}Cl}\\ |\\ \mathrm{Cl}\end{array}$$

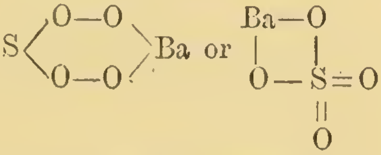
Roscoe has shown that uranium, which has hitherto been regarded as an artiad, forms a pentafluoride; he has also established that both the tungsten hexachloride (WCl_6) and the pentachloride (WCl_5) afford normal vapour densities. These facts clearly indicate that the elements are not capable of that rigid division into groups of odd and even atomic value which has hitherto been supposed.

It has already been observed that the atomic value of an element varies with the mode or phase of its existence. Our modern notions of the nature of heat prepare us to believe that the mutual affinities of two bodies may vary with the temperature, and it will be evident from the numerous examples given of abnormal vapour densities and dissociation that, as a rule, the atomic value of an element decreases with rise of temperature. This will be seen in the case of the sulphur chlorides; the power possessed by chlorine of holding atoms of chlorine in combination is greatest at low temperatures. There is also some evidence that the power of an element to hold other atoms in stable union depends upon the weight of the atoms so held. This fact is seen in the case of the pentahaloid derivatives of phosphorus; of the three known compounds, the fluoride is the most stable and the bromide the least stable.

But even when we have apparently satisfied the prevailing atomic value of an element by allocating to it what we assume to be the necessary complement of atoms of other bodies, it is frequently evident that the combining capacity of the whole molecule is not saturated. How otherwise can we explain the power which many apparently saturated molecules have of combining with other equally saturated molecules, as seen for example in the existence of such a body as zircon ($ZrO_2.SiO_2$), or in the formation of double salts, or in the combination of water with salts? It is possible in certain cases that this combination of apparently saturated molecules may be due to the re-arrangement of the mode in which the affinities are satisfied; thus in the combination of sulphur trioxide and barium oxide to form barium sulphate we may have:

Before combination: $SO_2=O$; or,  $O=\underset{\overset{\|}{O}}{S}=O$, and $Ba=O$.

Sulphur trioxide. Barium monoxide.

After combination: 

Barium sulphate.

We cannot, however, so explain the combination observed at low temperatures of two molecules of water with a molecule of sodium chloride, or the union of silver chloride with ammonia, or that of platinic chloride with hydrogen chloride, and numerous other cases of similar nature.

The relations between the properties of the elements and their atomic weights have been pointed out by various observers, and have recently been greatly developed by

Mendelejeff, who has shown that when the elements are arranged in the order of their atomic weights, the relations between these values and their chemical and physical properties exhibit the form of periodic functions. Thus, if we arrange the elements whose atomic weights are comprised between 7 and 36 in this manner, we have—

Li=7 Gl=9·4 B=11 C=12 N=14 O=16 F=19
Na=23 Mg=24 Al=27·3 Si=28 P=31 S=32 Cl=35·5.

The properties of these elements vary regularly and periodically with the increase in their atomic weight, and the corresponding members of the several series resemble one another in properties; thus Li is analogous to Na, Gl to Mg, B to Al, and so on. The atomic value of the elements periodically increases and diminishes with the atomic weight; thus Li is a monad, Gl a dyad, B a triad, C a tetrad, N a triad, O a dyad, F a monad, and a similar increase and diminution in atomic value is exhibited by the corresponding elements Na, Mg, etc. Similar relations are exhibited by the *specific volumes* of these elements:

	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Sp. gr.	0·97	1·75	2·50	2·49	2·20 (red)	2·00	1·33 (liquid).
Sp. vol.	24	14	11	11	14	16	27.

The other elements can in like manner be arranged in groups of small or *short periods* of seven, the members of which exhibit relations similar to those of the above groups (Mendelejeff.) The Table on the following page shows the elements arranged in the order of their atomic weights.

The members of the even series (4, 6, 8, etc.) manifest, on the whole, strongly marked basic properties, and yield no volatile hydrides or compounds with alcohol radicles; on the other hand, the members of the uneven series (3, 5, 7, etc.) exhibit, generally speaking, acid characters, and combine for the most part with hydrogen and alcohol radicles. In this respect, however, the second series is anomalous, since most of its members possess acid properties and combine with hydrogen and alcohol radicles. But this series is exceptional in other respects: the atomic weights of its members differ from those of the corresponding elements in the following series by only 16, whereas in the other series this difference

Typical Elements.							
			K = 39	Rb = 85	Cs = 133	.. ..	.. ..
			Ca = 40	Sr = 87	Ba = 137	.. ..	.. ..
			.. ..	? Yt = 88 ?	? Di = 138 ?	Er = 178 ?	.. ..
			Ti = 48 ?	Zr = 90	Ce = 140	? La = 180 ?	Th = 231
			V = 51	Nb = 94	.. ..	Ta = 182	.. ..
			Cr = 52	Mo = 96	.. ..	W = 184	U = 240
			Mn = 55	.. ..	.. ..	.. ..	.. ..
			Fe = 56	Ru = 104	.. ..	Os = 195 ?	.. ..
			Co = 59	Rh = 104	.. ..	Ir = 197	.. ..
			Ni = 59	Pd = 106	.. ..	Pt = 198 ?	.. ..
H = 1	Li = 7	Na = 23	Cu = 63	Ag = 108	.. ..	Au = 199 ?	.. ..
	Gl = 9,4	Mg = 24	Zn = 65	Cd = 112	.. ..	Hg = 200	.. ..
	B = 11	Al = 27,3	.. ..	In = 113	.. ..	Tl = 204	.. ..
	C = 12	Si = 28	.. ..	Sn = 118	.. ..	Pb = 207	.. ..
	N = 14	P = 31	As = 75	Sb = 122	.. ..	Bi = 208	.. ..
	O = 16	S = 32	Se = 78	Te = 125 ?	.. ..	.. ..	.. ..
	F = 19	Cl = 35,5	Br = 80	I = 127	.. ..	.. ..	.. ..

On re-arranging them in Series, we obtain the following Table:—

Series.	Group I. — R^2O.	Group II. — RO.	Group III. — R^2O^3.	Group IV. RH^4 RO^2.	Group V. RH^3 R^2O^5.	Group VI. RH^2 RO^3.	Group VII. RH R^2O^7.	Group VIII. — RO^4.
1	H=1							
2	Li=7	Gl=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P 31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=55, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	? La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — —

varies from 24 to 28. The difference between the atomic weights of successive even series is about 46, but in the elements of the second and fourth it ranges from 32 to 36. According to Mendelejeff, the anomalies exhibited by the members of the second series are related to these differences and afford further evidence of the interdependence of the atomic weight and properties of an element. On account of their exceptional character, Mendelejeff calls the members of the second series *typical elements*, by which term they are designated in the Table on page 33; in the fact of their exceptional properties they resemble the lowest members of many homologous series, which frequently fail to exhibit all the properties of the higher homologues.

Mendelejeff has applied these relations of periodicity among the atomic weights of the elements (1) to their classification; (2) to the determination of the atomic weights of little known elements; (3) to the prediction of the existence of other elements, of their properties and mode of occurrence; (4) to the rectification of doubtful atomic weights; and, lastly (5) to the extension of our knowledge of the forms of combination of compounds.*

In this book the elements are classified according to their predominant atomic values, that is to say, in accordance with the quantivalence indicated by the majority of their most stable and best defined compounds. Such a method of classification is not free from objection, but it serves, perhaps, better than any other yet devised to bring out the analogies and relations of the elements.

In the accompanying Table the elements are arranged in natural groups or families, so as to illustrate their prevailing atomic values and the numerical relations which exist between their atomic weights. It would seem to be highly probable that we may have correlated groups of various degrees of quantivalence. The character of the sequences exhibited by the elements is very remarkable, and strengthens our belief in the existence of undiscovered elements.

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* *Ann. der Chem. u Pharm.*, Suppl. VIII., p. 133; see also *Watts' Dictionary*, Suppl. II., p. 462.

MONADS.		DYADS.		TRIADS.		TETRADS.		PENTADS.		HEXADS.	
Hydrogen,	1	—	—	—	—	—	—	—	—	—	—
Fluorine,	19	Oxygen,	16	Nitrogen,	14	Carbon,	12	—	—	—	—
Chlorine,	35·5	Sulphur,	32	Phosphorus,	31	Silicon,	28	—	—	—	—
Bromine,	80	Selenium,	79·5	Arsenic,	75·2	—	—	—	—	—	—
Iodine,	126·9	Tellurium,	128	Antimony,	122·3	Tin,	118	—	—	—	—
Lithium,	7	Glucinum,	9·3	Boron,	11	—	—	—	—	—	—
Sodium,	23	Magnesium,	24	—	—	Aluminium,	27·3	—	—	—	—
Potassium,	39·1	Calcium,	40	? —	—	—	—	—	—	—	—
Rubidium,	85·4	Strontium,	87·5	? Yttrium,	88	Zirconium,	89·6	Niobium,	94	Molybdenum,	95·8
Cæsium,	133	Barium,	137·2	? Didymium,	138	Cerium,	138·0	—	—	—	—
						Lanthanum,	139				
—	—	—	—	—	—	Titanium,	50	Vanadium,	51·3	Chromium,	52·1
—	—	Copper,	63·4	—	—	Cobalt,	58·7	—	—	Manganese,	54
—	—	Zinc,	65·2	—	—	Nickel,	58·7	—	—	Iron,	56
Silver,	108	Cadmium,	112	Indium,	113·4	[? Tin,	118]	—	—	—	—
—	—	Palladium,	106·6	Rhodium,	104·2	—	—	—	—	Ruthenium,	104·4
—	—	—	—	? Erbium,	178	—	—	Tantalum,	182·3	Tungsten,	184
—	—	Mercury,	200	Gold,	197	Platinum,	197·2	—	—	Osmium,	199·1
—	—	—	—	—	—	Iridium,	196·9	—	—	—	—
Thallium,	203·6	—	—	Bismuth,	210	Lead,	207	—	—	—	—
—	—	—	—	—	—	Thorium,	231·5	—	—	Uranium,	237·6

CHAPTER II.

SPECTRAL ANALYSIS—ELECTRO-CHEMICAL DECOMPOSITION.

The spectroscope has acquired such importance in chemical research that it is necessary to give some account of the principles upon which it is based, of the modes of its application, and of the chief facts to which it has led, so far at least as these relate to chemical science.

Light is a result of molecular motion. The molecules of a luminous body are in a state of vibration, the rapidity of which varies with the degree of luminosity. This vibration is communicated to the *ether*, a highly elastic medium of great tenuity pervading all space; the ether is thus thrown into waves, to the amplitude and duration of which, as they strike the retina, are due the intensity and colour of the light. The rapidity of the oscillations producing the different degrees of colour observed in particular parts of the solar spectrum, and the corresponding lengths of the ether waves, are contained in the following Table :—

Colour.	No. of oscillations in one second of time.	Length of Waves in millionths of a millimetre.
Red, - - -	477 billions.	650
Orange, - -	506 ,,	609
Yellow, - -	535 ,,	576
Green, - -	577 ,,	536
Blue, - -	622 ,,	498
Indigo, - -	658 ,,	470
Violet, - -	699 ,,	442

The number of undulations corresponding to the various colours is inversely proportional to their wave-lengths; the most rapidly vibrating and shortest waves are those which excite the sensation of violet; the most slowly vibrating and longest waves are those which produce the sensation of red.

White light is the effect of waves of different lengths and times of oscillation all transmitted at the rate of 186,000 miles in a second. On passing such light through a prism, the various portions of it are bent out of the original rectilinear course, some more than others, so that if the emergent and now decomposed light be allowed to fall upon a white screen we observe a succession of bands of colour without sharp lines of demarcation; such a series of coloured bands is called a *spectrum*. The waves which are least bent out of the original course are those corresponding to the red, those which are most diverted are the violet, and the position of the intermediate rays follows the order of diminishing wave lengths given in the Table.

The spectrum afforded by white light extends considerably beyond the limits commonly visible, and by special appliances it can be shown that both at the red and at the violet end are vibrations which make little or no impression on the retina under ordinary conditions. On account of their difference in wave length and rapidity of vibration the various rays producing a spectrum are capable of bringing about very different effects; the rays which are mainly concerned in giving the impression of light are comprised between the edges of the red and blue in the spectrum, the maximum effect being caused by those corresponding to the yellow; the more refrangible rays are specially concerned in chemical actions, as in the decomposition of silver salts or in the combination of chlorine and hydrogen, whilst the less refrangible rays bring about the effects of heat. The maximum heating effect is produced by vibrations outside the visible limit of the red, whereas, on the other hand, the maximum amount of chemical action results from rays at the confines of the visible violet.

The *spectroscope* is an instrument in which the vibrations of the molecules of luminous bodies, transmitted by means of the ether, are analysed. The ether vibrations are disentangled, so to say, and sorted into appropriate position, and are received directly upon the retina of the observer. Fig. 1 represents an ordinary chemical spectroscope.

The light emitted from the glowing substance enters the instrument through a narrow slit and passes along the *colli-*

mator tube A, the lens in which makes the rays parallel; the rays then pass through the prism P (the edge of which is placed parallel to the slit) whereby they are decomposed; the decomposed light is received upon the eye of the observer placed at the end of the telescope B. Suppose now we pass through the slit ether vibrations of a certain definite wave-length, these are bent out of their direct course in passing through the prism, and we see a representation of the slit more or less magnified in accordance with the greater or less magnifying power of the telescope. Suppose now we send through the slit another set of definite vibrations differing from the last, we obtain a second image of the slit, but in another part of the field; the position of the two images with respect to one another depending upon the wave-lengths and refrangibilities of the two sets of vibrations. For the same reason the colours of the two images will vary. If, now, we pass through the slit vibrations of very different wave-lengths, we shall have as many different images of the slit as we have definite sets of vibrations. If we pass white light, which contains all sorts of vibrations, through the slit, we obtain so many images that it becomes impossible to trace any

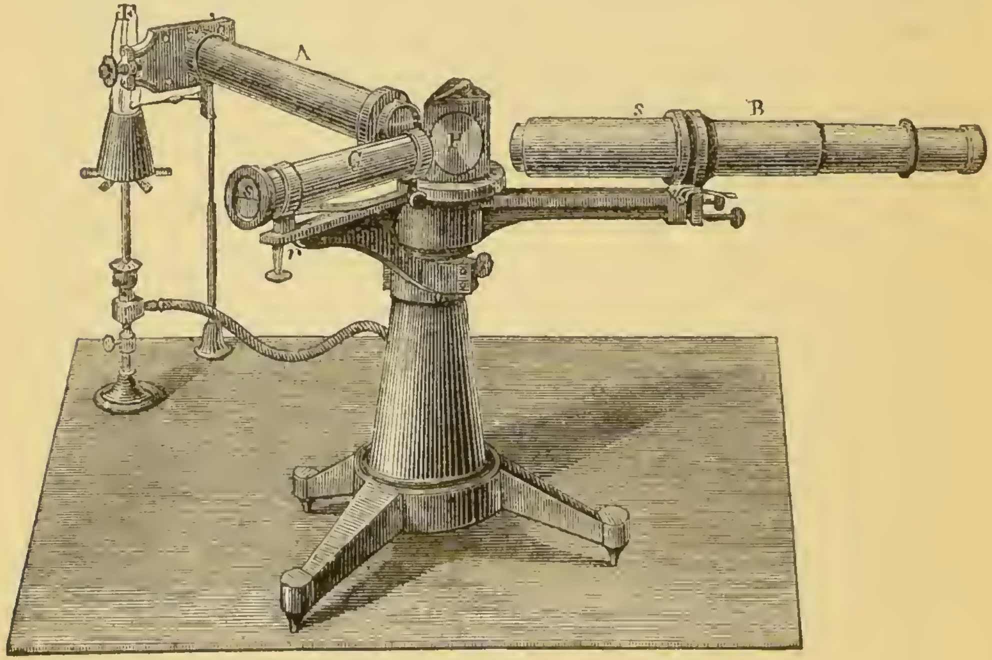

Fig. 1.

dark intervals between them; we have thus a continuous spectrum.

We know of certain lights corresponding to definite wave-lengths: the light from incandescent sodium is of this character; its wave-length is about $\frac{1}{589}$ millionth of a millimetre, and it affects us with the sensation of yellow. Hence if we pass these vibrations through the prism, we perceive only a yellow representation of the slit. The light emitted from glowing thallium has also a definite wave-length, viz., $\frac{1}{535}$ millionth of a millimetre, and is, therefore, monochromatic. It produces the sensation of green. We have, therefore, a green image of the slit. If, now, we simultaneously introduce into a flame compounds of thallium and sodium, and examine the mixed light by means of a prism, we shall observe a yellow and a green representation of the slit each in its appropriate position. Many compounds of barium colour the flame a peculiar yellowish-green; if this light be examined by the spectroscope, a number of coloured images of the slit are seen which, if the slit be made very narrow by the adjusting screw, seen on the end of the collimator tube, appear as bright lines. Hence the light emitted from incandescent barium is composed of sets of vibrations of very varying wave-lengths and rapidity of oscillation. These barium lines always occupy the same relative position, and, consequently, they may be employed to recognise that element. A number of other bodies also propagate vibrations which are constant in character for the particular substance even under widely divergent conditions, and hence the lines which they afford in the spectroscope may be employed for their detection. To examine a substance by means of the spectroscope, a small bead of it, supported on the unlooped end of a thin platinum wire, is brought within the fusion zone of the non-luminous gas flame, and the light emitted is viewed through the telescope. In the tube C is a photographic copy of a millimetre scale, an illuminated image of which is reflected from the anterior side of the prism P into the telescope, and is thus seen in the field of vision; upon this illuminated scale, the position of the several lines afforded by the body under examination may be registered. The brilliancy of the lines increases with the temperature, and at an intense heat, additional lines frequently make their appearance, due probably to the fact that the vibrations to which they correspond are too feeble to render themselves visible at low temperatures. Occasionally the heat of the Bunsen flame is insufficient to effect the volatilization of the element, and the high temperature of the electric spark is requisite. A succession of induction sparks, made more vivid by means of an intercalated Leyden jar, is caused to pass between poles consisting of the body under examination, particles of which are torn off and rendered incandescent; the emitted light is sent through the spectroscope and examined in the same manner as that from a flame. If the spark passes in air the spectrum contains lines due to oxygen, nitrogen, and hydrogen (from the decomposition of aqueous vapour), in addition to those arising from the glowing metal; but since the positions of the air lines are constant, and can be definitely established, it is readily possible to pick out those lines which properly belong to the element under examination. From their number, constancy, and the ease with which they may be obtained, these air lines are frequently employed as reference lines in spectroscopic research.

A very convenient mode of producing these spark-spectra has been described by Bunsen; it consists in saturating little carbon cones made from hard, well-burnt charcoal (previously surrounded with charcoal powder and heated to whiteness, and freed from silica lime, iron, etc., by boiling with acids), with a solution of the body under examination. The cones are supported on platinum wire inserted in corks sliding on glass rods, so that the points can be readily adjusted before the slit of the spectroscope. The induction current passes from the little mercury cup *a*, through the fine wire *b* to the carbon point *c*, and hence as a spark to the opposite carbon point (fig. 2). A small mica plate is placed immedi-

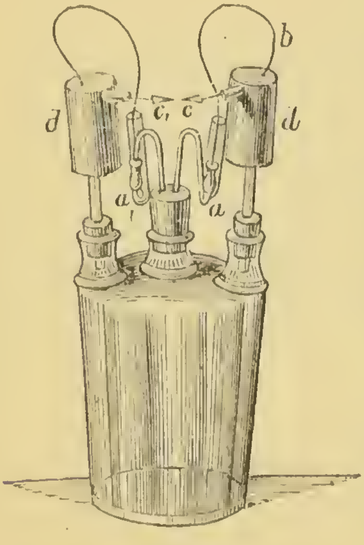

Fig. 2.

ately before the slit to prevent the projection of particles of the liquid through it.

As a rule, a compound such as sodium chloride or thallium sulphate, when heated in the non-luminous flame of the Bunsen lamp, emits light of the same character as that afforded by the metal itself, although exceptions to the rule are numerous. Thus the flame-spectrum of calcium chloride is very different from that yielded by the metal at the high temperature of the electric spark, and the light emitted by magnesium burning in air yields a spectrum due partly to the metal and partly to the oxide.

In examining gases, the induction discharge is made to pass through the rarefied gas contained in tubes fitted with platinum electrodes. The light emitted from a gas is in many cases found to vary with the tension of the electrical discharge. Thus, in the case of nitrogen, a low electric tension gives a spectrum consisting of bands and bright striæ; with high tension, a spectrum of narrow bright lines is obtained—these are termed respectively *spectra of the first and second order.* Under increased pressure, and with a high tension discharge, certain gases emit light of all degrees of refrangibility, and hence afford continuous spectra.

Of all processes of qualitative analysis, spectral analysis is by far the most delicate and sensitive, and exceedingly minute quantities of substances may be detected by its means. The method has revealed the presence of many comparatively rare bodies in substances in which otherwise no trace of them would have been recognised, and it has already added five new metals to the list of the elements, the names of which, with the exception of the last discovered, are derived from certain peculiarities of their spectra:—

Name.	Date of Discovery.	Discoverer.
Rubidium, - -	1859	Bunsen.
Cæsium, - -	1859	,,
Thallium, - -	1861	Crookes.
Indium, - -	1863	Reich and Richter.
Gallium, - -	1875	Lecoq de Boisbaudran.

The instrument has proved of great service in many branches of physical science, and, as applied to the analysis of the light emitted from heavenly bodies, it has afforded results of the highest importance.

On examining sunlight by means of the spectroscope, it is noticed that the bright continuous spectrum is crossed by a number of fine black lines of very different intensities of blackness and degrees of refrangibility. These lines were first observed by Wollaston, and made the subject of special study by Fraunhofer, after whom they have been named. Fraunhofer, who mapped the lines, assigned distinguishing letters to the more prominent of them; he noticed that one of the lines, that marked D in his map, was absolutely coincident in position with the bright yellow line obtained from glowing sodium. It is readily possible to demonstrate this coincidence by allowing sunlight to enter through one portion of the slit and the light from incandescent sodium to pass through the other. The mode in which this may be effected will be clear from fig. 3. A right-angled prism is placed before the lower portion of the slit through which the sodium light coming from B is sent by total reflection into the collimator, whilst direct sunlight passes through the upper portion of the slit. Two spectra placed one above the other are seen, and it will be remarked that the bright yellow sodium line forms an exact continuation of the dark D line in the solar spectrum. Hence this dark D line and the yellow sodium line must have the same wave-length and rapidity of oscillation.

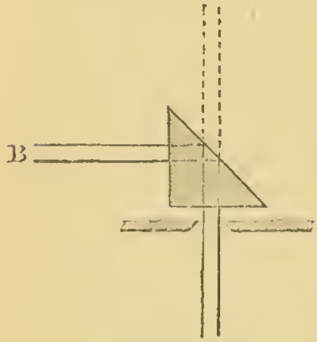

Fig. 3.

If we pass the light from glowing hydrogen through the comparison prism, we observe three characteristic lines: one in the red, a second at the less refrangible edge of the blue, and a third at the other limit of the blue; these lines are exactly coincident with three dark lines in the solar spectrum, known respectively as C, F, and G. The light emitted from incandescent iron particles yields a highly-complicated spectrum, containing upwards of four hundred lines, each of which coincides in position with a dark line in the solar spectrum. Some of the lines in the iron spectrum are brighter than others, and some are sharper and better defined. The brighter and more distinct the iron line, the blacker and more distinct is the Fraunhofer line; if the edge of the bright iron line is indistinct, the edge of the coincident dark line is correspondingly ill-defined.

Now it is in the highest degree improbable that coincidences of this character can be accidental; it is almost certain that there is some connection between the bright lines of the sodium, hydrogen, and iron spectra, and the corresponding Fraunhofer lines. This connection was first traced by Kirchhoff. The dark Fraunhofer lines corresponding to the bright lines of sodium, hydrogen, and iron, are due to the presence of these elements in the solar atmosphere. Comparisons of the line spectra of other elements with the Fraunhofer lines have further indicated the existence of the following substances in the sun : aluminium, magnesium, calcium, strontium, barium, chromium, nickel, cobalt, zinc, cadmium, copper, manganese, and titanium.

But we have to explain why the lines which in the ordinary spectrum appear bright upon a dark ground, are seen in the solar spectrum to be dark upon a bright ground. If we bring before a broad and sufficiently hot flame containing glowing sodium vapour, and therefore coloured strongly yellow, a second, but smaller and cooler flame, also containing vapour of sodium, it will be noticed that the smaller flame appears almost black when seen against the bright background of the larger flame. If we place a sodium flame before the slit of the spectroscope, we, of course, see the yellow line corresponding to the line D in the solar spectrum; if now we place an ordinary candle flame behind the sodium flame we shall see the bright sodium line upon a comparatively faint continuous spectrum. By substituting the electric light for the candle flame, the continuous spectrum becomes intensely bright, whilst the sodium line appears by contrast to be nearly black, since only that portion of the spectrum which is covered by the sodium line is made luminous by the sodium flame. The glowing sodium gas has, in fact, arrested those rays which it itself emits; that is, it is nearly opaque for rays of its own kind, whilst it is perfectly transparent to rays of other refrangibility. If instead of sodium we place thallium or lithium in the flames precisely the same result follows; the same kind of vibrations are stopped which are emitted, and the spectra are, as it is termed, *inverted.* Now, according to Kirchhoff, the sun is an extremely hot mass emitting white light. Surrounding the white-hot core, or *photosphere,* is an atmosphere of glowing vapour of sodium, hydrogen, iron, calcium, etc., through which the light of the photosphere has to pass. Precisely the same action goes on as in the flames; exactly those vibrations are arrested in the gaseous envelope or *chromosphere* which it emits; hence the production of black lines instead of the bright lines we should see if we could examine the outer atmosphere alone, or if the luminous orb had a much lower temperature. A number of the Fraunhofer lines, those marked *a* and B for example, are, however, due to the absorptive action of the aqueous vapour in the earth's atmosphere; this is indicated by the fact that these lines are most distinctly seen at low altitudes of the sun, and when therefore its light has to traverse the greatest extent of terrestrial atmosphere. The validity of Kirchhoff's explanation of the Fraunhofer lines has been placed beyond doubt by the fact discovered by Lockyer and Jannsen, that the bright instead of the dark lines may be obtained by viewing the edges of the sun's disc, that is the chromosphere, by means of a powerful dispersing spectroscope. Indeed, during a total solar eclipse, when the light from the photosphere has been entirely cut off by the dark disc of the moon, and the chromosphere has been alone visible, the whole of the dark Fraunhofer lines have been seen to change suddenly to bright lines.

On comparing the bright line spectrum of certain elements with the dark Fraunhofer lines, it occasionally happens that certain of them show no correspondence with lines in the solar spectrum. `This is due to the fact that both the number and length of the lines in the spectra of metallic vapours depend upon the density of the absorbing or radiating medium, only the longest lines remaining visible when the vapours are rarefied. Lockyer has shown that the inverted lines in the solar spectrum correspond to the longest lines observed in the spectrum of each element. The presence of zinc and aluminium in the sun is established by the fact that the lines corresponding to these elements are the longest lines in the spectra of their vapours.

An examination of the light of the fixed stars has shown that the general character of their atmospheres is the same as that of the sun, although remarkable differences have been observed between individual stars. The spectroscope has also rendered it highly probable that both the nebulæ and comets are simply masses of self-luminous gases, since they afford line spectra.

6. Absorption Spectra.—If a ray of sunlight or of the electric light be passed through nitrogen peroxide, the emergent light yields a spectrum containing an immense number of dark lines. This phenomenon is due to the same cause as that by which the Fraunhofer lines are produced; the gas, although at the ordinary temperature, has, like the aqueous vapour in the atmosphere, arrested certain vibrations, and allowed others to pass. From the loss of these vibrations the emergent light is no longer white; but the gas appears of a reddish-yellow colour, since the less refrangible rays are allowed to pass in greatest number. The violet colour of iodine vapour, and the reddish-yellow of bromine and of iodine chloride are due to a similar cause; these vapours have the power of arresting certain vibrations, whereby the colour of the emergent light is modified. Many coloured liquids, such as potassium bichromate and permanganate, an alkaline solution of the green colouring matter of plants (chlorophyll), blood, litmus, etc., yield characteristic absorption spectra. Absorption lines differ from the greater number seen in the solar spectrum, or from the bright lines of the spectra of glowing metals, inasmuch as they are not definite images of the slit. The breadth of the lines is increased by increasing the thickness of the absorbing medium, and certain colours are seen to disappear gradually, so that the colour of the object varies with the thickness of the layer through which the light is transmitted.

Remarkable absorption spectra are afforded by solutions of the salts of didymium and erbium; a liquid containing the former metal yields two dark lines in the yellow, and two in the green. If the solid oxide of didymium be rendered incandescent, *bright* lines are obtained in exactly the same position as the dark lines afforded by the solution. Solutions of erbium behave in like manner; they afford absorption lines which are exactly the reverse of the bright lines given by the incandescent oxide. These two bodies are exceptional in this respect; no other *solid* substance is known which yields a line spectrum on heating.

ELECTRO-CHEMICAL DECOMPOSITION.

We have already seen that a voltaic current in traversing certain compound liquids effects their decomposition; for example, water acidulated with sulphuric acid is resolved into oxygen and hydrogen, and hydrochloric acid into chlorine and hydrogen. Such a process of decomposition is termed *electrolysis.* We noticed, moreover, that the same elements are always evolved at the same pole or *electrode;* thus the hydrogen was invariably evolved from the plate in connection with the zinc of the battery, that is, from the negative pole; the oxygen and chlorine, on the other hand, were always evolved from the plate in connection with the carbon or platinum, that is, from the positive pole. All liquid bodies cannot be thus decomposed, since all do not conduct; for example, many organic liquids as alcohol and ether, and certain inorganic bodies are unchanged by the action of the current. Many saline substances, as silver and lead chlorides, experience electrolytic decomposition when fused, but are absolutely unacted upon when solid. An aqueous solution of a salt may be electrolysed; hence it appears that a certain freedom of motion of the molecules is necessary before electrolytic decomposition can occur.

The electric current appears to exert a directive action or polarising effect upon the atoms of bodies; thus in the decomposition of hydrochloric acid, the hydrogen atoms move with the positive current towards the negative pole, whilst the chlorine atoms travel in the opposite direction. The most careful examination of the liquid between the two poles fails however to reveal the presence either of free chlorine or of free hydrogen; these gases are first observed in the immediate neighbourhood of the electrodes. It is assumed, therefore, that the hydrogen and chlorine atoms in passing to the electrodes suffer a series of alternate decompositions and combinations. Thus in fig. 4, let *d* be a molecule of hydrochloric acid, situated midway between the two electrodes; under the influence of the current it is decomposed, the hydrogen atom travelling towards the negative electrode combines with the chlorine of the molecule *c*, the hydrogen of which combines with the chlorine of *b*, its hydrogen combines with the chlorine of *a*, and *a*'s hydrogen makes its appearance at the plate; a similar series of decompositions and combinations leaves the chlorine of *g* at the positive electrode. Indeed it is possible that this decomposition and recombination of the constituent atoms of hydrochloric acid may be proceeding within the liquid, even under ordinary conditions, and that the current merely exerts a directive action upon the bodies.

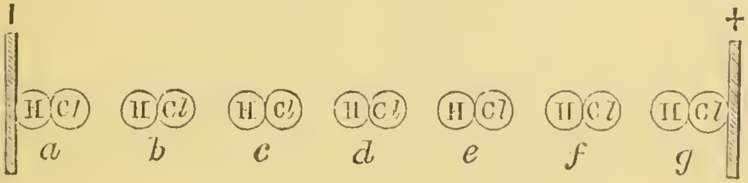

Fig. 4.

If we dip the electrodes into *pure* water, very little action takes place; on adding a few drops of sulphuric acid a rapid disengagement of gas occurs, oxygen appears at the positive pole, and hydrogen at the negative pole. The sulphuric acid is probably split up into H_2 and SO_4, a hypothetical group of atoms which has received the name of *sulphion*. The molecule of hydrogen, by a series of transformations similar to that described in the case of hydrochloric acid, reaches the negative pole, and the sulphion group the positive pole. In the moment of liberation, however, at the pole the sulphion decomposes water with the liberation of oxygen:

$$H_2O + SO_4 = SO_4H_2 + O.$$

Hence the result is the same as if the water were alone electrolysed; one volume of oxygen from the water is disengaged from the positive pole, and two volumes of hydrogen from the acid at the negative pole.

Many substances in solution are similarly decomposed: thus common salt yields its chlorine at the positive pole, and its sodium at the negative pole. In contact with water, however, metallic sodium is converted into caustic soda with the evolution of free hydrogen:

$$H_2O + Na = NaHO + H.$$

The sodium hydrate remains dissolved and hydrogen is liberated.

Sodium hydrate, however, is readily capable of decomposition by voltaic electricity. If a piece of the hydrate made moist by deliquescence be placed in the circuit of a powerful current by laying it on a plate of platinum connected with the positive pole of the battery, and a platinum wire connected with the negative pole be inserted into the softened mass of the alkali, oxygen gas is rapidly evolved at the plate, and small metallic globules of sodium of a silvery white lustre make their appearance round the wire. This experiment was first made by Davy in 1807; he showed that caustic potash and certain of the earth-hydrates were similarly decomposed. The electrolytic decomposition of potassium hydrate may be readily demonstrated by placing a small quantity of mercury at the bottom of a flat dish (fig. 5), and dipping into it a stout platinum wire, covered with sealing-wax as far as the horizontally bent portion, and connected with the negative end of the battery. On pouring over the mercury a quantity of strong potash solution, and placing in it a small piece of sheet platinum connected with the positive pole, decomposition rapidly ensues, and in time the mercury becomes solid from the formation of potassium amalgam.

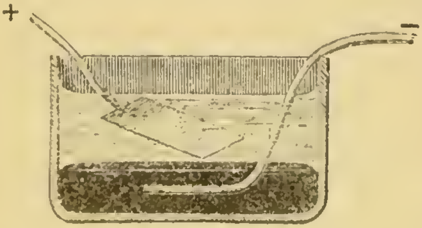

Fig. 5.

Magnesium may be readily obtained in small quantity by the electrolytic decomposition of its melted chloride, by means of the simple apparatus seen in fig. 6. An iron wire is pushed down the stem of a clay tobacco-pipe into the bowl, which is then filled with a mixture, in equal proportions, of magnesium and potassium chlorides. Such a mixture fuses at a lower temperature than either chloride singly, and when fused is specifically lighter than metallic magnesium; the separated metal is thus retained beneath the surface of the fused mixture and is preserved from oxidation. When the mixture is fused, a piece of gas carbon connected with the positive pole of a few platinum-zinc or carbon-zinc elements is introduced into it, the iron wire being connected with the negative end of the battery. Chlorine is rapidly evolved from the carbon, and on breaking the pipe after half-an-hour's continuance of the current, a globule of magnesium may be found in the solidified saline mass.

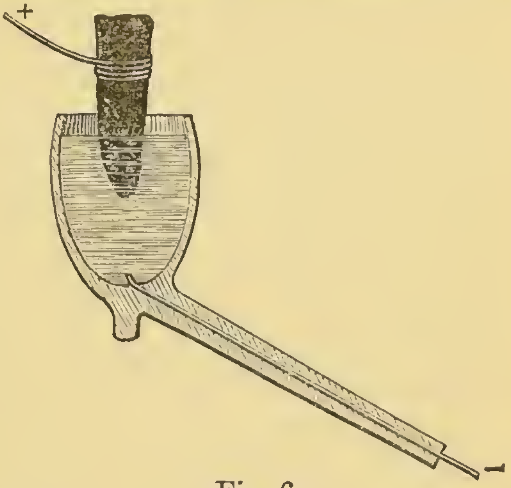

Fig. 6.

A solution of copper sulphate is readily electrolysed, copper being deposited at the negative pole and oxygen evolved at the positive pole; the sulphion (SO_4) decomposing water at the moment of liberation, as in the electrolysis of sulphuric acid. The decomposition of copper sulphate is made use of in copying medals, and in the production of electrotypes from the wood-engraver's blocks. An impression from the medal or from the wood-block is made in wax or some similar material, which is then brushed over with finely-powdered graphite, and suspended in a solution of copper sulphate. The wire from the positive end of the battery is attached to a copper plate dipping into the copper sulphate solution; to the other wire is attached the wax mould. Copper is gradually and uniformly deposited upon the mould, and the liberated SO_4 dissolves the copper from the plate, so that the strength of the solution remains unimpaired; the SO_4 under the influence of the current transfers the copper of the plate to the mould. Provided that the mould has been carefully made, and that its surface is evenly coated with black-lead, the engraver's work may be produced with great fidelity, and from the toughness of the metal any number of impressions may be taken from the electrotype. In a similar manner, gold, silver, platinum, and other metals, may be deposited from their solutions. The article to be *electroplated* is suspended in a bath of the appropriate solution, together with a plate of the same metal which is to be deposited.

It is necessary to distinguish between electrolysis proper and its secondary effects. Thus, in the foregoing illustrations, the oxygen produced in the electrolysis of sulphuric acid is the result of the secondary action of the group SO_4 upon water; in like manner the hydrogen evolved in the electrolysis of sodium chloride is formed by the action of the liberated sodium upon water. The electrolysis of a concentrated solution of sal-ammoniac affords an additional example of secondary action. Hydrogen is evolved from the negative pole, but neither oxygen nor chlorine is liberated from the positive pole; after some time, however, this electrode is seen to be covered with oily drops of so-called nitrogen terchloride, produced by the action of the free chlorine upon the ammonium chloride.

Electrolytic oxygen, especially in the moment of liberation, is capable of bringing about many phenomena of oxidation; thus a solution of potassium valerianate under its influence yields the hydrocarbons octane and butene, together with carbon dioxide and hydrogen. If a solution of lead or manganese acetate be electrolysed, the dioxides of lead or manganese are deposited upon the positive electrode; these oxides are formed by the action of the evolved oxygen upon the protoxides in solution.

By passing the same current through a number of different *electrolytes*, *i.e.*, substances capable of electrolytic decomposition, it will be noticed that each is simultaneously decomposed; and if the quantities of the separated elements be determined, it will be seen that they have been set free in the ratio of their chemical equivalents. Thus, supposing the electrolytes were acidulated water, silver chloride, lead chloride, and stannous chloride, for each part by weight of hydrogen evolved from the water at the negative electrode we should have 108 parts of silver, 103·5 parts of lead, and 59 parts of tin, at the other negative electrodes; and for every 8 parts of oxygen at the positive electrode in the water, we should have 35·5 parts of chlorine at each of the other positive electrodes. The amount of chemical decomposition which the current is able to produce is strictly proportionate to the amount of circulating electricity; hence, from the extent of decomposition occurring in an electrolyte, we may obtain a measure of the electrical force needed to produce a given effect. On this principle Faraday constructed the *voltameter*, an instrument in which the amount of gas evolved from acidulated water in a given time by the current is measured. If, now, we turn to the battery in which the electrical disturbance originates, it will be found that the amount of chemical decomposition produced in the electrolyte is strictly proportionate to the chemical decomposition in the battery, as measured by the quantity of zinc dissolved; thus for every milligram of hydrogen evolved in the voltameter, 32·6 milligrams of zinc are dissolved. As a matter of fact, however, this result is seldom obtained in practice, since it is almost impossible to prevent what is termed *local action* in the battery, which leads to an increased consumption of zinc. If a piece of ordinary commercial zinc be placed in dilute sulphuric acid, it is rapidly dissolved, and hydrogen is evolved. On the other hand, perfectly pure zinc is very slowly acted upon by the acid; the rapid action in the case of the ordinary metal is due to the production of numbers of voltaic currents from the presence of impurities in the metal. This local action may be almost entirely prevented by coating the zinc plates with mercury.

It was formerly believed that all chemical phenomena were the result of electrical action, and that the combination and decomposition of bodies resulted from differences in their electrical condition. Accordingly, the elements have been arranged in a series depending upon the tendency they manifest during electrolysis to make their appearance at one or other of the electrodes; those which appear at the positive electrode are termed *electro-negative elements;* those which appear at the negative electrode are *electro-positive elements.* The following Table gives the electro-chemical order of the elements; each element is electro-negative to those following it:—

—
Oxygen.
Sulphur.
Selenium.
Nitrogen.
Fluorine.
Chlorine.
Bromine.
Iodine.
Phosphorus.
Arsenic.
Chromium.
Boron.
Carbon.
Antimony.
Silicon.
Hydrogen.
Gold.
Platinum.
Mercury.
Silver.
Copper.
Bismuth.
Tin.
Lead.
Cobalt.
Nickel.
Iron.
Zinc.
Manganese.
Aluminium.
Glucinum.
Magnesium.
Calcium.
Strontium.
Barium.
Lithium.
Sodium.
Potassium.
Cœsium.
Rubidium.
+

The relative position of a number of the elements in this Table is still a matter of doubt, since in the case of some of them it has been only indirectly determined. If we arrange the bodies as in the Table on page 35, it will be seen that each element is electro-negative to those following it, and electro-positive to those which precede it; the electro-chemical position of a member in the family group appears therefore to be a function of its atomic weight.

CHAPTER III.

CRYSTALLOGRAPHY.

The great majority of bodies exhibit a tendency to *crystallise,* that is, to assume regular polyhedral forms, when their molecules are free to take up positions of equilibrium. Some substances, as gelatin, albumin, and the like, are apparently devoid of symmetrical arrangement, whilst a third group, of which starch may be taken as the type, show a distinct *organised* structure, perfectly different in character from that of a crystal.

A *crystal* is a body of symmetrical form, bounded by plane surfaces, produced by separation from solution, by the solidification of a fused mass, or by sublimation, sometimes without intermediate liquefaction. We have already observed many examples of the modes in which crystals are generated. Thus an aqueous solution of sodium chloride deposits that salt in *cubes;* melted sulphur solidifies in long *prisms,* and arsenic trioxide sublimes in *octahedrons.*

As a general rule, each substance has a characteristic crystalline form, although instances are by no means rare in which two perfectly distinct bodies have a common crystalline shape; such substances are said to be *isomorphous.* Not unfrequently the same body possesses two distinct crystalline forms; it is then termed *dimorphous.* Occasionally two substances crystallise in the same two forms; they are then said to be *isodimorphous.*

When we examine a number of crystals of the same substance, say of rock-crystal, a very superficial observation shows us that although there may be no absolute identity of form among them, in a geometrical sense, there is yet sufficient analogy of shape to make it certain that they have *essentially* the same figure. The immediate cause of the divergence in form is in the unequal development of corresponding planes; this will be apparent from figs. 7, 8, 9, and 10, which represent crystals of quartz. It is evident that the different appearances of the crystals are due to differences in the areas of corresponding planes or *faces.*

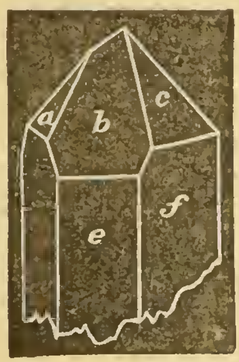

Fig. 7.

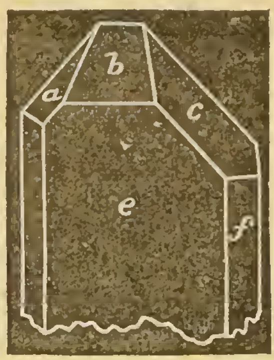

Fig. 8.

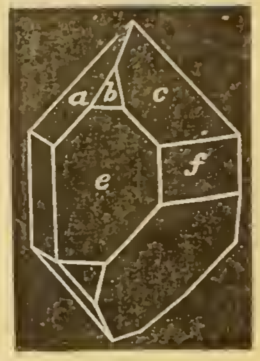

Fig. 9.

If now we attempt to construct a form from such crystals in which all the corresponding faces shall be equally developed, we obtain a crystal similar to that represented by fig. 11, that is, *a six-sided prism terminated by six-sided pyramids.* But on examining natural crystals, similar to those above represented, it is noticed that however different their form may seem, the angle made by the approximation of two corresponding faces (that is, the *interfacial angle*) is always the same, no matter what may be the relative size of the faces. Thus, the angle of *b* upon *c* is invariably 133° 14′, and that of *e* upon *f* invariably 120°. Crystals of quartz (rock-crystal) analogous to that represented by fig. 11 are occasionally met with, but this, the ideal form, is more frequently departed from. Indeed, this is equally true of most crystallised substances. Fig. 12 represents a form frequently assumed by lead nitrate and by alum; the ideal form of the crystal is a regular octahedron; the mode in which the abnormal crystal is derived from the fundamental form will be seen by reference to fig.

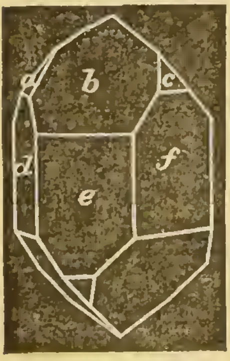

Fig. 10.

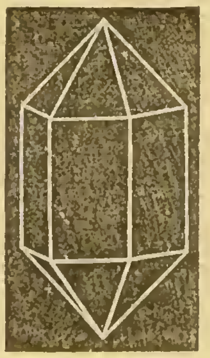

Fig. 11.

13. Although the faces of the octahedron are so unequally developed, the interfacial angles are exactly the same as in the ideal crystal.

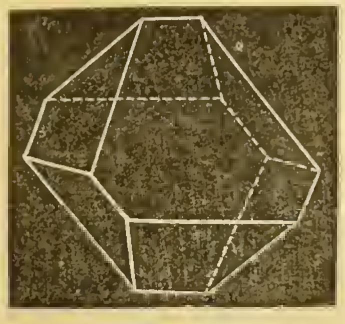

Fig. 12.

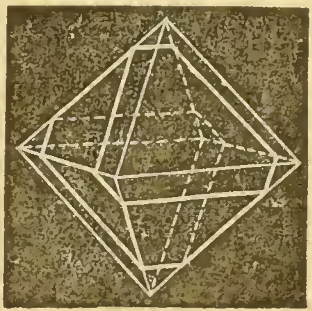

Fig. 13.

On examining a perfect crystal of quartz or of alum, it becomes evident that each crystal may be conceived as symmetrically arranged around certain imaginary lines, or *axes*, to which the several faces may be referred. Thus, in the regular octahedron (fig. 14), we may conceive *three* such axes joining the opposite angles. In the quartz crystal we have *four* axes—one running through the entire length of the crystal and joining the summits of the pyramids, and three at right angles to the vertical axes, and ending either in the middle or at the edges of the prismatic faces.

Every crystal yet discovered can be referred to one of six different systems, distinguished by differences in the relative position and comparative length of the axes. These systems are as follows:—

I. The *Regular* system, in which the crystals are grouped around *three* axes of equal length, placed at right angles to each other. From the equality in the length of the axes, this system is also termed the *isometric* or *monometric* system.

II. The *Quadratic* system, in which are *three* axes placed at right angles to each other. Two only of the axes are equal in length, the third may be longer or shorter than the other two. Since two of the axes are of the same length, this system is also known as the *dimetric;* and from the fact that a section cut in the plane of the two equal axes would form a square, it has also been termed the *tetragonal* system.

III. The *Hexagonal* system has *four* axes, three of which are equal, lie in the same plane, and cut each other at an angle of 60°; the fourth axis may be longer or shorter than the other three; it cuts them at their common point of intersection at a right angle. This system is sometimes termed the *rhombohedral* system, since the rhombohedron is one of its most important derivatives.

IV. The *Rhombic* system has *three* axes of unequal length placed at right angles to each other. It is also called the *trimetric* system, from the inequality in the length of the three axes.

V. The *Monoclinic* system has *three* axes of unequal length, one of the axes stands at right angles to the plane of the other two, which are inclined to one another at different angles in different crystals.

VI. The *Triclinic* system has *three* axes, no one of which makes a right angle with either of the other two.

I. The Regular System.

The regular octahedron (fig. 14) may be regarded as the fundamental form of this system; the axes connect together the opposite solid angles. This body has eight equilateral triangular faces; it has six angles, each of which is formed by four edges, and is in all respects similar to the others; in all, it has twelve perfectly equal edges. The points in which these meet are equidistant from the centre of the crystal where the three axes cut one another; the semi-axes or *parameters* are therefore equal, and, accordingly, each octahedral face cuts the three axes at an equal distance from the centre.

The several faces of a crystal may be distinguished by reference to the distance from its centre at which each face cuts the different axes; as we have seen, each face of the regular octahedron cuts each axis at an equal distance from the centre; hence if we represent this distance by a, we may distinguish the face by the formula $a : a : a$, or, more shortly, by the symbol O.

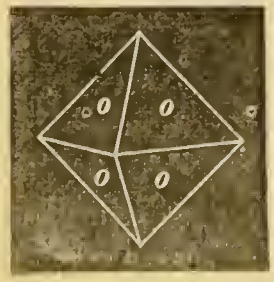

Fig. 14.

The regular octahedron is one of the commonest crystallographic forms; the following bodies among others assume it: Sodium, magnesium, cadmium, iron, lead, copper, mercury, silver, gold; many alloys and amalgams of these metals; certain of their oxides; arsenic trioxide; and the oxides of the spinel group. Among the salts may be mentioned the alums, the nitrates of lead, barium, and strontium; the chlorates and bromates of nickel, cobalt, and copper, zinc, and magnesium; the chlorides of silver, ammonium, lithium, and, occasionally, sodium; certain double chlorides and cyanides, and the pentahydrated borax.

It is a general law that like parts of a crystal are similarly, unlike parts dissimilarly modified; hence, since all the angles on the octahedron are precisely similar, it follows, that when any one is altered in any way, all the others are altered in the same manner. Thus each angle may be replaced or *truncated* by a face, as seen in fig. 15; by the gradual development of this face (marked *a* in the figures), we obtain the forms seen in figs. 16 and 17, and if we conceive the faces to grow until all trace of the octahedral planes are lost, we obtain the *cube*, fig. 18. Fig. 15 represents a *combination* of the octahedron and cube; fig. 17 a combination of the cube and octahedron: the dominant face being first stated in describing the crystal. In fig. 16 the axes of the crystal end in the middle of the cubical faces; they are exactly half the length of those of the primitive octahedron, and the faces of the two forms meet in points only. Since this crystal stands midway in the passage of the one form into the other, it is termed the *middle-crystal.*

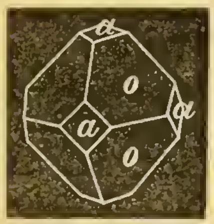

Fig. 15.

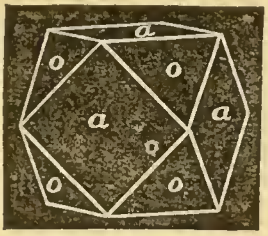

Fig. 16.

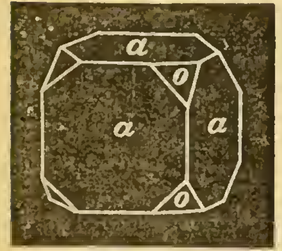

Fig. 17.

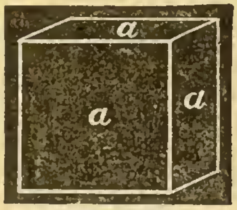

Fig. 18.

If we regard the cube as derived from the octahedron, and assume that the absolute position of the axes is unaltered, it is evident that each face will cut only one of the axes and will run parallel to the other two; that is, it will cut them only at an infinite distance: we may therefore distinguish this face by the formula $a : \infty a : \infty a$, or, shortly, by the symbol $\infty O \infty$.

Many substances which crystallise in octahedrons are found to crystallise also in cubes, or in combinations of the cube and octahedron. Such substances are not said to be dimorphous, unless they also crystallise in forms belonging to some other system.

The following bodies show a special tendency to assume the cubical form: Fluor-spar, galena, speiss-cobalt, arsenical cobalt, manganese, silver, and iron sulphides, nickel and cobalt glance, and the alkaline chlorides, bromides, and iodides.

Suppose, now, we truncate the edges of the octahedron: since these are similar in all respects, it follows that any modification we make on one edge will extend to the other eleven. Fig. 19 represents an octahedron with truncated edges, marked *d*. By the development of the truncating planes, we obtain the form seen in fig. 20, and if these planes be supposed to extend until the octahedral faces disappear, we have the form represented by fig. 21, known as the *rhombic dodecahedron*. This body is bounded by twelve similar rhombic faces; it has twenty-four similar edges, eight of its fourteen solid angles are three-sided, the remaining six being four-sided. Each face cuts two axes at equal distances from the centre, and is parallel to the third; accordingly, it may be designated by the formula $a : a : \infty a$, or by the symbol ∞O.

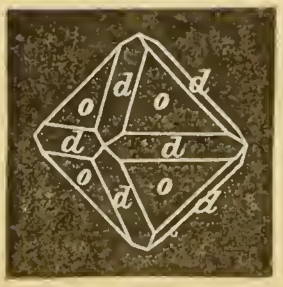

Fig. 19.

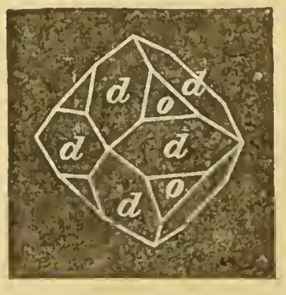

Fig. 20.

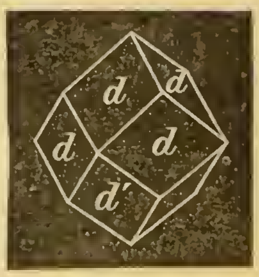

Fig. 21.

Fig. 19 shows a combination of the octahedron and the dodecahedron; fig. 20 a combination of the dodecahedron and octahedron.

The rhombic dodecahedron, both alone and in combination with the cube and octahedron is observed on phosphorus, copper, silver, and gold; on native silver-amalgam, cuprous oxide, zinc-blende, galena, silver-glance, fahl-ore, fluor-spar, and garnet. It is not very common on artificial crystals, but has been noticed in combination on potassium iodate, on alum, on sodium-uranium acetate, and on potassium and sodium chlorides.

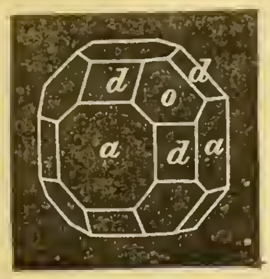

Fig. 22.

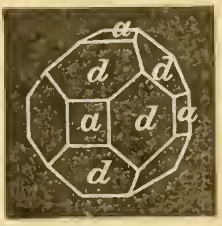

Fig. 23.

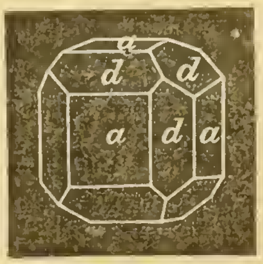

Fig. 24.

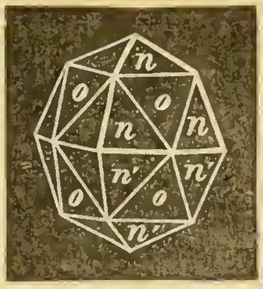

Fig. 25.

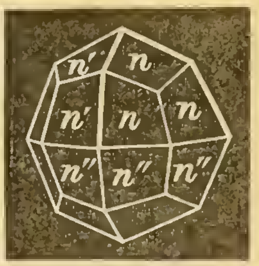

Fig. 26.

The remaining forms of this system are still less frequently observed on artificial crystals; some of them, however, constitute the characteristic forms of certain important minerals.

Let us suppose that on each cubical face of the combination $O . \infty O \infty$ seen in fig. 16 (p. 57), a four-sided pyramid be placed, the height of which is half the diagonal of its base; we thus obtain the form represented in fig. 25.

If we now assume that each set of the four pyramidal faces is equally developed until the faces of the octahedron disappear, we get the form represented in fig. 26, and termed the *deltohedron* or *ikosi-tetrahedron*. In this particular form each face cuts one axis at the distance a, and the other two at twice that distance; accordingly it may be represented by the symbol $a : 2a : 2a$, or by $2O2$.

If we suppose that a more obtuse pyramid be placed on the cube face of the combination seen in fig. 16, and that the same process of development takes place as in the previous case, we obtain a second form of the deltohedron. Thus, if the height of the pyramid were only $\frac{1}{3}$ of the half-diagonal of the base, we should get faces cutting the axes in the relation of $a : 3a : 3a$: this form would have the symbol 3O3. Deltohedrons have been observed on analcime, garnet, iron-pyrites, and galena; and on native gold and silver; they have also been noted in combination on ammonium chloride, and on chrome and common alum.* Fig. 25 represents an alum crystal of the combination O.2O2.

Suppose that on each face of the simple cube (fig. 18) a four-sided pyramid be placed, we thus obtain the form seen in fig. 27; it is known as the *four-faced cube* or *tetrakis-hexahedron.* Each face runs parallel to one axis, cuts the second at the distance a, and the third at $\frac{3}{2}a$, $2a$, $\frac{5}{2}a$, $3a$, or $5a$, depending upon the steepness of the pyramid. It may therefore be represented by the general formula $a : ma : \infty a$, or $m\text{O}\infty$; the forms actually observed having the symbols $\frac{3}{2}\text{O}\infty$, $2\text{O}\infty$, $\frac{5}{2}\text{O}\infty$, $3\text{O}\infty$, and $5\text{O}\infty$. These forms have been noticed on native gold and silver, and, generally subordinate to the cube, on fluor-spar (see fig. 28). They have also been observed in combination on sodium sulphantimoniate, and on rock-salt.

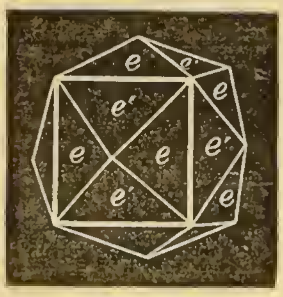

Fig. 27.

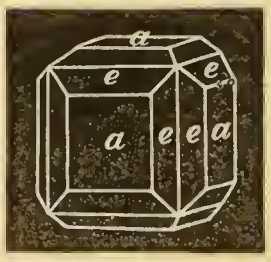

Fig. 28.

If we assume that on each face of the regular octahedron a three-sided pyramid be placed, we obtain the form seen in fig. 29; it is termed the *three-faced octahedron* or *triakis octahedron.* Each face cuts two axes at an equal distance from the centre, and the third at some greater distance; its general formula is

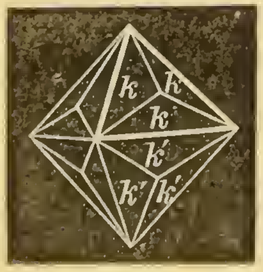

Fig. 29.

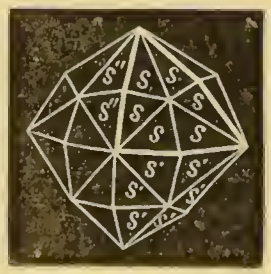

Fig. 30.

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* Leucite was formerly supposed to have the form 2O2; it has been shown, however, by Vom Rath to belong to the quadratic system (see p. 64).

therefore $a : a : m a$, or mO: the particular cases (mainly noticed on the diamond, galena, and pyrites) are $\frac{3}{2}$O, 2O, and 3O.

Lastly, if on each face of the octahedron a six-sided pyramid be placed, we obtain the *six-faced octahedron* or *hexakis octahedron*, seen in fig. 30. Each face of this form meets the three axes at unequal but finite distances from the centre. The general formula is therefore $a : ma : na$, or mOn. The most commonly occurring forms are 3O$\frac{3}{2}$ and 2O4; the former has been noted on garnet, and the latter on fluor-spar. The diamond and cuprite also occur in these forms.

II. Quadratic System.

The *quadratic octahedron*, the fundamental form of this system, is distinguished from the regular octahedron by having two only of its three axes equal, the third being sometimes greater, sometimes less, than the other two. The variable or *principal* axis is assumed to be vertical in representations of quadratic crystals; denoting it by c the general formula of a quadratic octahedron is $a : a : c$, or mP. The relation of the principal to the lateral axes, although very different in different substances, is constant for the same body. Fig. 31 represents the fundamental octahedron of potassium ferrocyanide in which the relation of the axes is as 1·77 to 1. Fig. 32 shows the primary octahedron of mercuric cyanide ($HgCy_2$), in which $c = 0·46$.

The eight faces of the quadratic octahedron form isosceles triangles. We have to distinguish two kinds of edges: those which lie in the plane of the lateral axes, marked *ss* in the figures, and termed *lateral edges*, which together form a square; and those which meet the vertical axes, marked *tt*, and termed the *polar edges*, which together form a rhomb. We have also to distinguish two kinds of angles: the *summit angles*, made by the meeting of similar sides, and the *lateral angles*, made by the meeting of dissimilar sides. As a result

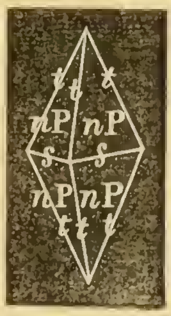

Fig. 31.

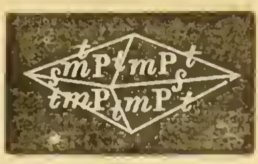

Fig. 32.

of the law of symmetry, we find that the summit angles may be truncated without the others. Since the *end-face* thus produced cuts the principal axis, and runs parallel to the two secondary axes, it may be designated by $c : \infty a : \infty a$, or by oP, as in fig. 33, which represents a form of potassium ferrocyanide.

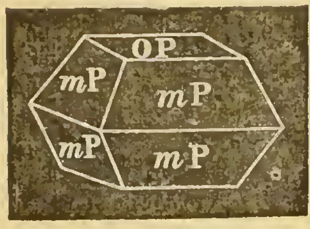

Fig. 33.

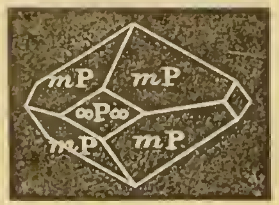

Fig. 34.

The lateral angles may also be alone truncated, as in fig. 34, which represents a crystal of potassio-cupric chloride ($2KCl.CuCl_2$). This face cuts one of the lateral axes, and runs parallel to the other and to the vertical axis; hence it has the formula $a : \infty a : \infty c$, or shortly, $\infty P \infty$, by which it is designated in the figure. If we suppose the four truncating faces $\infty P \infty$ to grow until they meet, we should obtain the *quadratic prism* (fig. 35), exactly as we obtained the cube from the regular octahedron in the preceding system. Fig. 36 represents a combination of the quadratic prism with the end-face.

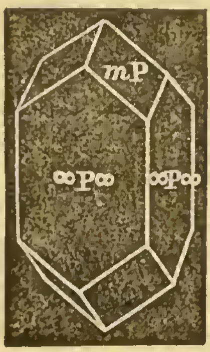

Fig. 35.

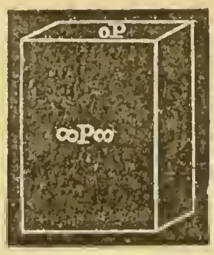

Fig. 36.

Let the four lateral edges of the quadratic octahedron be replaced by faces; this replacement can, of course, occur without the polar edges being altered; we thus obtain the combination seen in fig. 37. Each of the truncating faces cuts the secondary axes at an equal distance from the centre, and runs parallel to the principal axis; hence it has the formula $a : a : \infty c$, or ∞P. The sign ∞ placed before P denotes that it refers to the principal axis; when placed after, it refers to the secondary axes. Fig. 38 represents a combination of the prism ∞P with the end-face

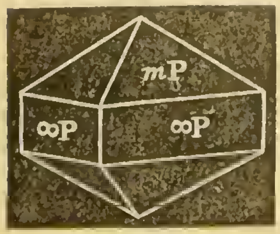

Fig. 37.

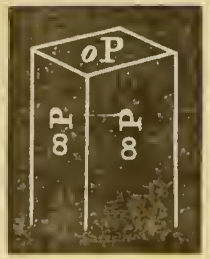

Fig. 38.

oP. We have thus two quadratic prisms: one obtained by the development of faces replacing the lateral angles of the octahedron; the other by the development of faces replacing the lateral edges. We may have a combination of the two prisms, as in fig. 39, which resembles the form of quartz without the pyramids. Fig. 40 shows a combination of the quadratic prisms first and second order, the octahedron and the end-face: both this form and that represented in the preceding figure are observed on copper-calcium acetate ($Cu.Ca.4C_2H_3O_2.SH_2O$.)

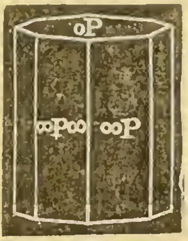

Fig. 39.

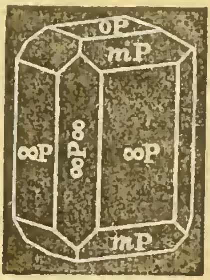

Fig. 40.

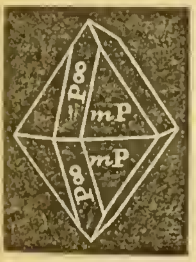

Fig. 41.

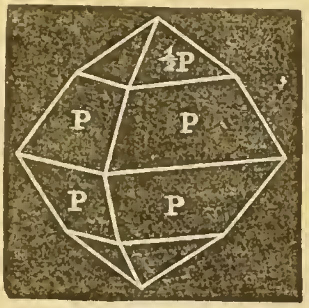

Fig. 42.

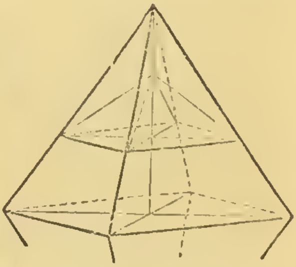

Fig. 43.

By truncating the polar edges of the quadratic octahedron, we obtain the combination seen in fig. 41. The replacing face runs parallel to one secondary axis, but cuts the other at the distance a, and the principal axis at the distance c; hence it has the symbol $a : \infty a : c$, or P∞ as in the figure. If these faces be uniformly developed until those of P disappear, we obtain a second quadratic octahedron: an octahedron which stands in the same relation to the original octahedron as the prism ∞P does to the prism ∞P∞. mP is termed an octahedron of the *first order;* P∞ an octahedron of the *second order.* Combinations of the two octahedra occasionally occur; the dominant octahedral faces are regarded as of the first order.

It frequently happens that the terminal summits of the quadratic octahedron are truncated by an obtuser pyramid, as in fig. 42. The height of the apex of the obtuser pyramid always stands in some simple relation to that of P, when both are measured from the same base. The relation of the particular obtuse pyramid in fig. 42 to P may be rendered clear from fig. 43. If the polar edges of P be considered to be prolonged until they meet, as seen in fig. 43, and the vertical axis be prolonged to the point of juncture of the four edges, it will be seen that the height of the obtuser pyramid is exactly half that of P when both are measured from the base of the obtuser pyramid; hence the designation of the latter of $\frac{1}{2}$P. We may have even more obtuse pyramids, as $\frac{1}{3}$P $\frac{1}{4}$P. . . $\frac{1}{n}$P. The shorter the vertical axis of $\frac{1}{n}$P the more obtuse the pyramid; when $\frac{1}{n} = o$ we have a horizontal plane, or the *end* or *basal face;* hence the designation *o*P already given to this face. Fig. 44 represents a combination of P, $\frac{1}{2}$P, and *o*P, occurring on nickel sulphate ($NiSO_4.6H_2O$). We may, however, have more *acute* pyramids than P, as 2P, 3P, 4P, etc., and just as on the one hand we pass over to the end-face *o*P by increasing the obtuseness of the pyramid, so, on the other, by increasing its acuteness, we pass over to the quadratic prism; hence its designation of ∞P. We have also obtuser and acuter pyramids than P∞, that is, of the second order, viz., $\frac{1}{3}$P∞, $\frac{1}{2}$P∞ . . . 2P∞, 3P∞. Fig. 45 represents a combination of P and 2 P∞ occurring on anatase (TiO_2). Fig. 46 represents a complicated form of nickel sulphate. Fig.

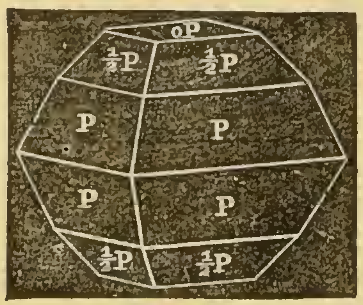

Fig. 44.

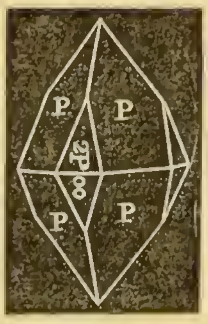

Fig. 45.

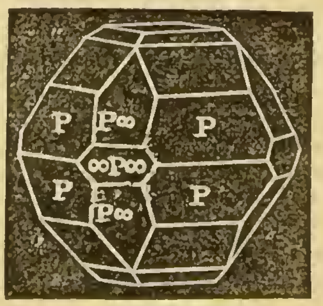

Fig. 46.

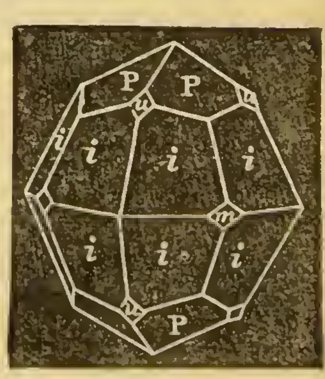

Fig. 47.

47 is a combination of P with an acuter octagonal pyramid or dioctahedron marked *i*, the acute octahedron $2P\infty$ marked *u*, and ∞P marked *m* are occasionally seen, but are generally very subordinate. These forms belong to leucite ($K_2O.Al_2O_3.4SiO_2$), a mineral which was formerly supposed to crystallise in the regular system.

The following bodies, in addition to those already mentioned, crystallise in forms derived from the quadratic system: tin, boron; tinstone (SnO_2); rutile (TiO_2); zircon (ZrO_2SiO_2), hausmannite (Mn_3O_4), and braunite (Mn_2O_3); copper pyrites, calomel; mercuric iodide (red modification), potassium phosphate (KH_2PO_4), vesuvian, and mellite ($C_6(CO_2)_6Al_2.18H_2O$).

III. Hexagonal System.

The fundamental form of this system is the double six-sided pyramid, fig. 48, the base of each pyramid is a hexagon (fig. 49), the lines *c d*, *e f*, and *g h* are the three equal and lateral axes; they intersect each other at the centre *m*, at an angle of 60°. The principal axis stands at right angles to the plane of the other three, and connects together the summits of the pyramids (fig. 48); it may be longer or shorter than the lateral axes. Each pyramidal face runs parallel to

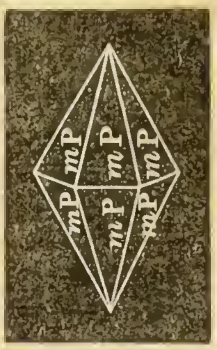

Fig. 48.

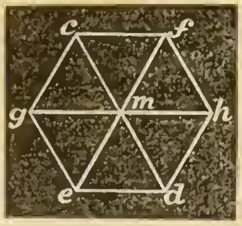

Fig. 49.

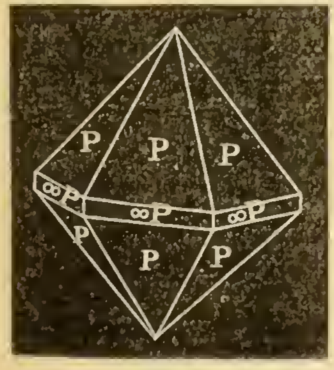

Fig. 50.

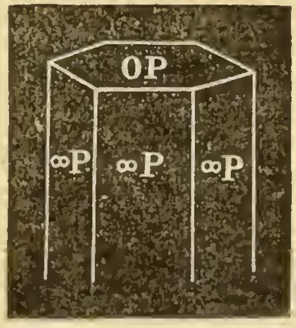

Fig. 51.

one secondary axis; hence, if we call the length of a secondary axis a, and that of the principal axis c, the face would have the formula $a : a : \infty a : c$, or P. Here, as in the quadratic octahedron, we have to distinguish two kinds of angles and sides, viz., the polar angles and sides, and the lateral angles and sides; and, as in that case, one set of angles or sides may be modified without the other. By replacing the six lateral edges by planes we obtain the combination seen in fig. 50; by the development of these planes we obtain the form seen in fig. 11, representing quartz. The truncated face runs parallel to the principal axis, and to one secondary axis; hence its formula is $a : a : \infty a : \infty c$, or ∞P; it is termed the *hexagonal prism.* Fig. 51 represents a combination of the hexagonal prism ∞P, with the basal or end face o P. Fig. 52 shows a crystal of beryl; it is a combination of ∞P, P, and *oP.*

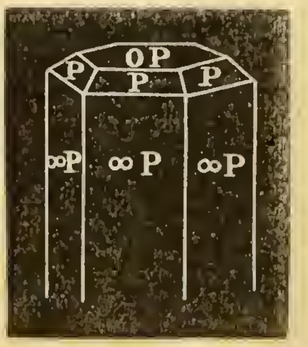

Fig. 52.

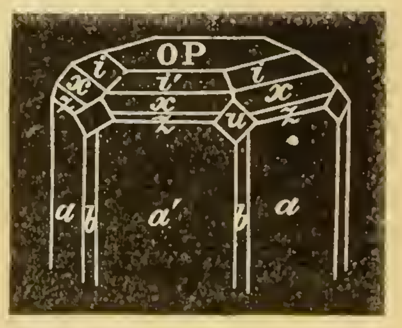

Fig. 53.

In this, as in the preceding system, we have obtuser and acuter pyramids than P, which may be represented by similar symbols, as $\frac{1}{3}$P, $\frac{1}{2}$P ... 2P, 3P, &c.; we have also pyramids and prisms of both first and second orders, designated as in the quadratic system. A number of these forms are seen in fig. 53, which represents a crystal of apatite. a = prism of first order ∞P; b = prism of second order ∞P2; i, x, and z, three pyramids of first order, u a pyramid of second order, and oP the basal plane.

The following bodies, in addition to those mentioned, crystallise in hexagonal pyramids or prisms, or in combinations of these forms: zinc, zinc oxide, silica as tridymite, magnetic pyrites (ferroso-ferric sulphide), nitrates of cæsium and rubidium, lithium sulphate, pyromorphite, vanadinite, and camphor.

IV. The Rhombic System.

The *rhombic octahedron*, figs. 54, 55, may be considered to be the primary form in this system; its three axes are situated at right angles to each other, but all are of unequal length; hence two rhombic octahedrons may have a very different habitus, depending upon the relative length of the different axes. Since all the axes are of unequal length, any one may be selected as the principal axis and placed vertically. As a rule, the principal axis is determined by the habitus of the crystal; that is, by the direction in which it is usually most developed; for example, in the prismatic forms, that axis which runs parallel to the longer edges of the prism is assumed to be the principal axis.

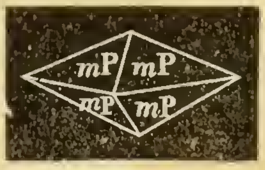

Fig: 54.

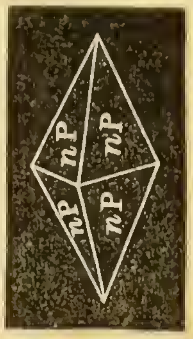

Fig. 55.

A section cut in the plane of any of the axes of the rhombic octahedron forms a rhomb; in the quadratic octahedron we can have either a rhomb or a square; in the regular octahedron we have only squares. In figuring a rhombic crystal, the axis selected as principal is vertical; the longer of the two secondary axes, termed the *macro-diagonal*, runs from one hand to the other, and the shorter secondary axis, termed the *brachy-diagonal*, is at right angles to the other: the principal axis and the macro-diagonal appear of their true relative length; the brachy-diagonal is fore-shortened. Representing the length of the brachy-diagonal by a, that of the macro-diagonal by b, and that of the vertical axis by c, the formula of the rhombic octahedron is $a : b : c$, or P.

Since each pair of opposite angles of the rhombic octahedron differs from the others, any two opposite angles may be modified without the others being altered. Thus we may have the upper and lower terminal angles alone truncated; since the truncating face stands at right angles to the principal axis, and is parallel to the secondary axes, it may be distinguished by the symbol $c : \infty b : \infty a$, or, as in the preceding system, and for the same reason, oP. Any symbol before P refers to the principal axis; any symbol after P to a secondary axis; if to the longer axis it is further distinguished by the sign —, if to the shorter by the sign ⌣. The truncating faces on the angles in which the brachy-diagonal ends are termed the *brachy-diagonal end-faces*, and, since they run parallel to the principal axis and to the macro-diagonal, they are distinguished by the symbol $\infty\bar{P}\infty$; conversely, the planes truncating the other lateral angles are termed the *macro-diagonal end-faces*, and have the symbol $\infty\breve{P}\infty$. Fig. 56 represents a combination of $\infty\bar{P}\infty$ and P; fig. 57 of $\infty\breve{P}\infty$ and P.

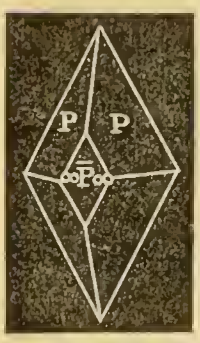

Fig. 56.

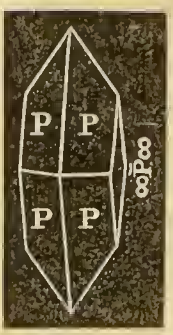

Fig. 57.

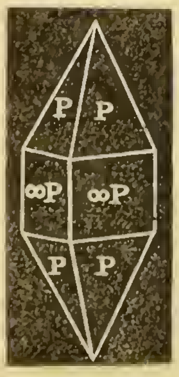

Fig. 58.

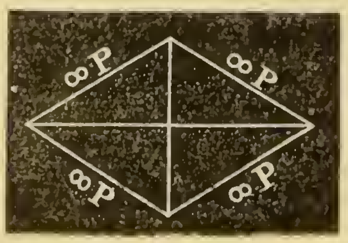

Fig. 59.

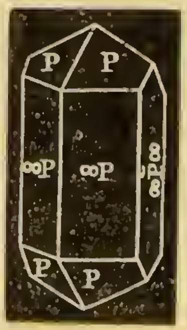

Fig. 60.

The twelve edges of the rhombic octahedron are divided into three groups; each group of four edges lying in the same plane, and together forming a rhomb, are of the same kind: we have the macro-diagonal polar edges, *i.e.*, those connecting the macro-diagonal and the principal axis; the brachy-diagonal polar edges which connect the brachy-diagonal and the principal axis; and lastly, the four horizontal edges lying in the plane of the secondary axis. By truncating the horizontal edges, we obtain a four-sided prism, (fig. 58) with rhombic base (fig.

59). Since the truncating faces run parallel to the principal axis, and cut the secondary axes at the distances a and b, its formula is $a : b : \infty c$, or ∞P. Fig. 60 represents a combination of ∞P, P, and the macro-diagonal end face $\infty \breve{P} \infty$, frequently observed on the sulphates of zinc and magnesium.

By truncating the four macro-diagonal polar edges of the octahedron, we obtain the combination seen in fig. 61, the replacing faces have the symbol $\breve{P}\infty$, since they run parallel to the brachy-diagonal axis, and cut the macro-diagonal at the distance b, and the principal axis at the distance c: they are termed *domes*, since they terminate in the vertical direction like the pitched roof of a house (*domus*). $\breve{P}\infty$ is the symbol of the *brachy-diagonal dome.* The macro-diagonal dome conversely has the symbol $\bar{P}\infty$. Fig. 62 represents a crystal of nitre, a combination of the prism ∞P, the brachy-diagonal end-face $\infty\breve{P}\infty$ and the brachy-diagonal dome $\breve{P}\infty$. Fig. 63 represents a crystal of barium formate of the combination ∞P and $\bar{P}\infty$; fig. 64 a combination of ∞P, P, $\breve{P}\infty$, $\bar{P}\infty$ and $\infty\bar{P}\infty$, seen on magnesium sulphate. In this, as in the two preceding systems, we have acuter and obtuser pyramids than P, distinguished by $\frac{1}{2}$ P, 2 P, etc. We have also acuter and obtuser domes, as $3\breve{P}\infty$, $\frac{1}{2}\breve{P}\infty$, etc., $3\bar{P}\infty$, $\frac{1}{2}\bar{P}\infty$, etc. We may also have prisms with variable horizontal sections: fig. 65 will serve to explain the manner in which these prisms

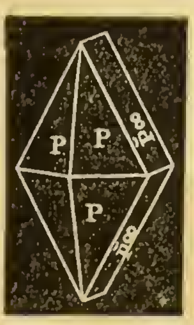

Fig. 61.

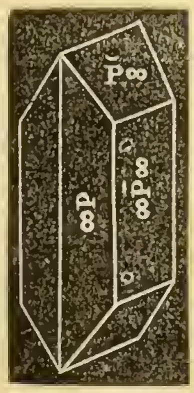

Fig. 62.

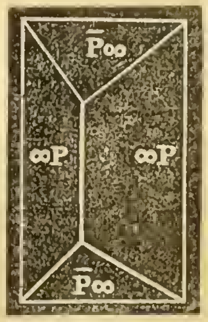

Fig. 63.

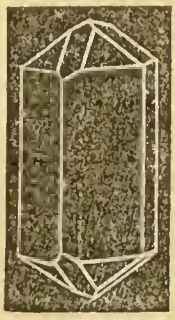

Fig. 64.

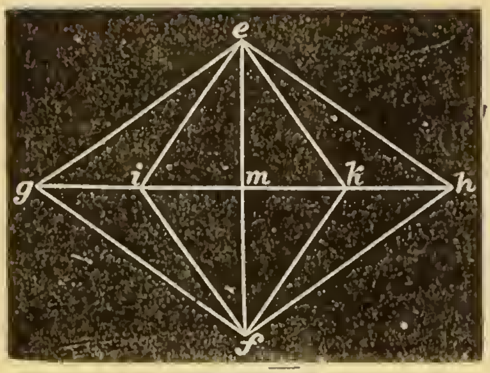

Fig. 65.

are designated. Let *e f*, *g h* be the secondary axes of the fundamental octahedron; the rhomb *g e h f* is the horizontal section of the prism ∞P. We may have other prisms derived from the same octahedron, in which *e f* is constant, but in which *g h* may be larger or smaller. Let the points *i* and *k* be situated midway between *g* and *m*, and *h* and *m* respectively; then *i e k f* is the ideal section of a prism, the diagonals of which are equal to the brachydiagonal, and half the macro-diagonal of the fundamental form. Such a prism would be designated by the formula $a : \frac{1}{2}b : \infty c$, or $\infty\bar{P}\frac{1}{2}$. Figs. 66 and 67 represent crystals of topaz: the first is a combination of ∞P, $\infty\bar{P}\frac{1}{2}$, and P; the second of $\infty\bar{P}\frac{1}{2}$, $P\infty$, and P. Fig. 68 is a combination of $\infty\breve{P}2$, and $\infty\breve{P}\infty$ and $\breve{P}$, observed on potassium sulphate; the crystal has been turned half-way round to show the position of the dominant faces. It will be noticed that the inclination of the edge between P and the prism $\infty P\infty$ varies with the value of n.

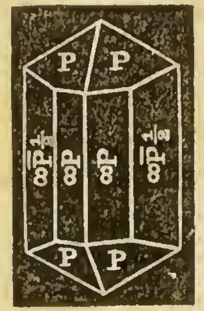

Fig. 66.

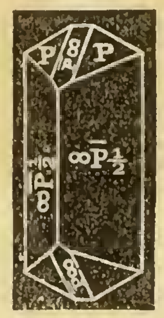

Fig. 67.

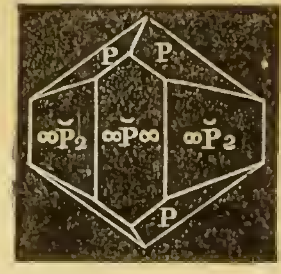

Fig. 68:

A large number of substances crystallise in this system; among these may be mentioned the chlorides of lead, barium, mercury, and copper; the nitrates of ammonium, and silver; the sulphates of ammonium, rubidium, sodium, silver, barium, strontium, and lead; and the carbonates of calcium (aragonite), barium (witherite), strontium, and lead.

V. THE MONOCLINIC SYSTEM.

In this system there are three unequal axes; two of which are obliquely inclined to one another; the third is at right angles to the others. One of the oblique axes is usually selected as the principal axis, since the majority of crystals belonging to this system are most developed in the direction of one of these axes. Of the secondary axes, that which is obliquely inclined to the principal axis, is styled the *clino-diagonal;* the remaining axis, *i.e.*, the one perpendicular to the other two, is termed the *ortho-diagonal.* In figures of monoclinic crystals the principal axis is vertical, the clino-diagonal runs from one hand to the other, and the ortho-diagonal from back to front; the inclination of the principal axis to the clino-diagonal is thus seen in the figure. This inclination is very different in different crystals: in ferrous sulphate ($FeSO_4.7H_2O$) it is 75° 40′; in sodium carbonate (Na_2CO_3, $10H_2O$) it is 57° 40′.

The fundamental form is the monoclinic octahedron (fig. 69) which, however, never occurs alone. It is bounded by eight scalene triangles, each meeting the axes at the distances *a*, *b*, and *c* from the centre. The faces are of two kinds, and are respectively designated as + P and – P; one set may occur without the other; or one set may be modified without the other set, if present, being altered. By varying the length of any one axis, we obtain other forms of octahedrons, as in the preceding system. The variation in the length of the principal axis is denoted by a sign placed before the P; a variation in the length of the secondary axes by a sign placed after the P. If the variation refers to the clino-diagonal the formula is enclosed in a bracket.

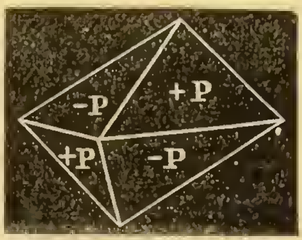

Fig. 69.

We may have octahedrons of the same base as P, acuter or obtuser than the primary form; they are distinguished by $+mP$ and $-mP$.

The oblique rhombic prism, very commonly observed on crystals in this system, is denoted by ∞P (fig. 70) when possessing the same base as P; oblique rhombic prisms of other bases than that of the fundamental form are designated by the general formulæ ∞Pn and $[\infty Pn]$. Fig. 71 shows a combination of the prism ∞P with $+P$ and the basal plane oP. Fig. 72 shows a combination of ∞P with $-P$ and oP.

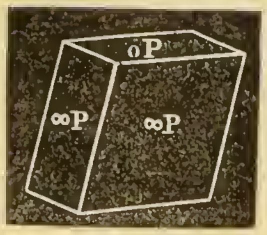

Fig. 70.

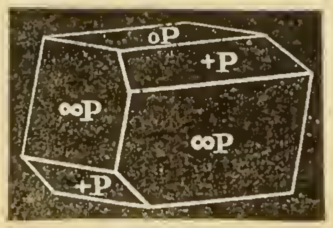

Fig. 71.

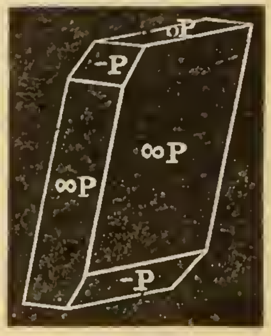

Fig. 72.

We have also pyramids on bases differing from that of P, and designated by mPn and $[mPn]$. The clino-diagonal domes $[P\infty]$ possess edges and faces running parallel to the clino-diagonal. The ortho-diagonal dome, the sides and edges of which run parallel to the ortho-diagonal, has the symbol $mP\infty$; it has four dissimilar faces denoted by $+mP\infty$ and $-mP\infty$, and either set of two may be present without the other.

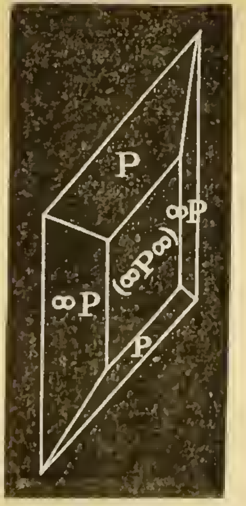

Fig. 73.

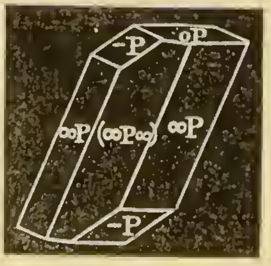

Fig. 74.

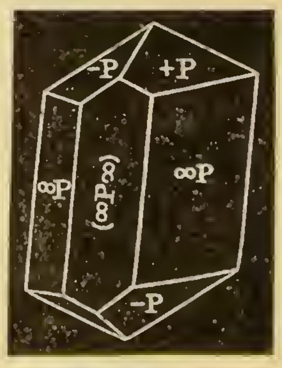

Fig. 75.

Lastly, we have clino-diagonal end faces cutting the ortho-diagonal, and running parallel to the clino-diagonal and principal axis denoted by $[\infty P\infty]$; the ortho-diagonal end-faces, which cut the clino-diagonal and run parallel to the ortho-diagonal and principal axis, are denoted by $\infty P\infty$.

Fig. 73 represents a combination of $-P$, the prism ∞P, and the clino-diagonal end-face $[\infty P\infty]$. Fig. 74 the same, with the addition of oP. Fig. 75 the same, with $+P$, but without the base. These forms are commonly observed on selenite.

Fig. 76 represents a crystal of the double sulphate of nickel and potassium; it is a combination of the prism ∞P, clino-diagonal dome $[P\infty]$, and basal plane oP. Fig. 77 is a combination of the ortho-diagonal dome $+P\infty$, the prism ∞P, the clino-diagonal end-face $[\infty P\infty]$, and the basal plane oP; it is a common form of ferrous sulphate. By undue development of the prismatic face, it often assumes a very different appearance; other forms of the salt are seen in figs. 78 and 79. Among the principal bodies crystallising in this system may be mentioned:—Sulphur, hydrated sodium chloride ($NaCl$ $2H_2O$), sodium carbonate ($Na_2CO_3.10H_2O$), potassium chlorate, sodium phosphate ($Na_2HPO_4.12H_2O$), the vitriols ($M.SO_4.7H_2O$), sodium thiosulphate, oxalic and tartaric acids, lead acetate, and cane sugar.

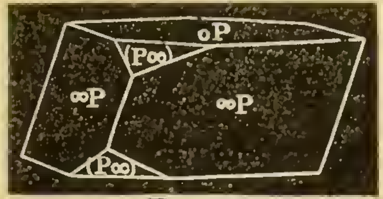

Fig. 76.

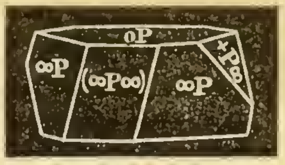

Fig. 77.

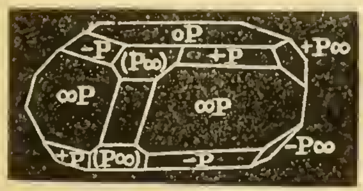

Fig. 78.

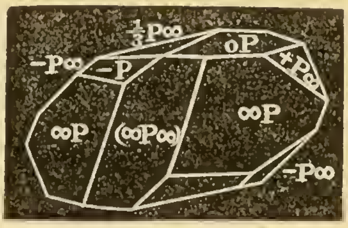

Fig. 79.

VI. Triclinic System.

All three axes in this system are obliquely inclined to one another, and (so far as is known) are unequal in length. The principal axis is selected as in the preceding system; the secondary axes—the macro- and brachy-diagonal—being placed in representations of the crystals so as to exhibit their peculiarities most clearly. The primary form may be regarded as an octahedron, the eight faces of which are of four kinds, each pair only of parallel faces being similar; hence each pair may occur in combination without the others. The six angles are of three kinds, and of the twelve edges only parallel pairs are similar. The complete octahedron (which, however, never actually occurs) is represented by the sign $'_{,}P_{,}'$; the four front faces are designated by $'P$, P', $_{,}P$, and $P_{,}$; the corresponding back faces being designated by the same signs (fig. 80). We have different octahedrons on the same base represented by the general formula mP, and octahedrons on different bases denoted by the general formulæ $m\bar{P}n$, and $m\breve{P}n$; each octahedron has the same variety of kinds of edges and faces as the primary form, and any two may occur without the others.

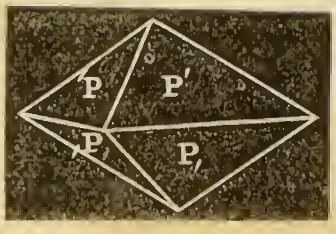

Fig. 80.

We have also triclinic prisms ∞P of the same base as the primary octahedron, and prisms of different bases denoted by $\infty\bar{P}n$ and $\infty\breve{P}n$; only parallel pairs of the four prismatic faces are similar, and either pair may occur in combination without the other. The right front face of the prism, and that behind which is parallel to it, are denoted by $\infty P'$, the others by $\infty' P$; the notation for the other prisms being similar. Domes parallel to the secondary axes are denoted by $m\bar{P}\infty$ and $m\breve{P}\infty$; the opposite faces are alone similar. The basal end-faces are denoted by oP, the brachy-diagonal end-faces by $\infty\breve{P}\infty$, and the macro-diagonal end-faces by $\infty\bar{P}\infty$.

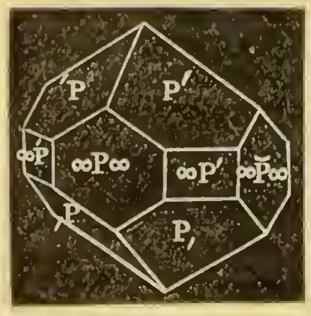

Fig. 81.

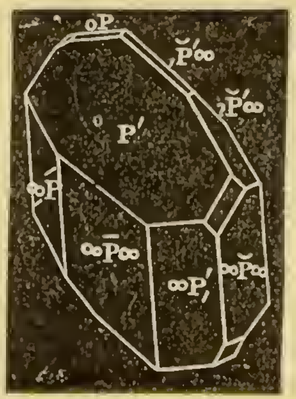

Fig. 82.

All triclinic crystals are necessarily combinations, and these are frequently highly complicated. Comparatively few salts crystallise in this system: among the chief substances may be mentioned copper, manganese, and iron sulphates, of the formula $MSO_4.5H_2O$; potassium and silver dichromates; boric acid and grape sugar. Figs. 81 and 82 represent characteristic forms of copper sulphate.

HEMIHEDRAL FORMS.

We have stated that not unfrequently the faces of a crystal are very unequally developed, and sometimes (as in the quartz crystals, figs. 7-10, p. 54, and in the crystals of lead nitrate, fig. 12, p. 55), certain of them are nearly wanting. This total disappearance of faces does actually occur in many cases, but according to law, and a body results of as symmetrical an ideal form as the fundamental one. Suppose, for example, four alternate faces of the regular octahedron were so extended, in the manner indicated by fig. 83, that the remaining four were nearly obliterated, we should obtain a form similar to that seen in fig. 84. If the four faces completely disappeared we should have the four-sided body, or *tetrahedron*, seen in fig. 85, and denoted by $\frac{O}{2}$ or $+\frac{O}{2}$. Of course, the other four sides might be developed in the same manner: we should thus obtain a second tetrahedron equally similar, but oppositely placed, and denoted by $\frac{O'}{2}$ or $-\frac{O}{2}$. Both tetrahedrons are occasionally found on the same crystal as in fig. 84.

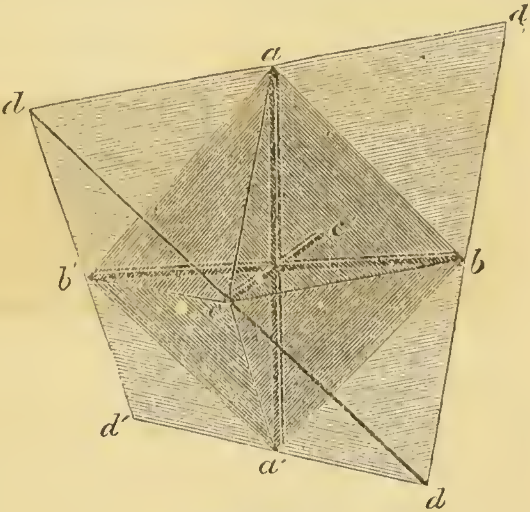

Fig. 83.

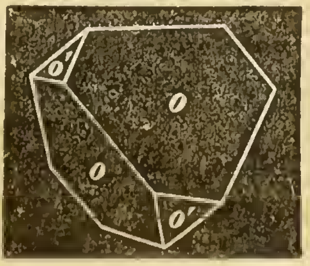

Fig. 84.

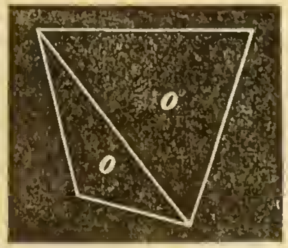

Fig. 85.

Such bodies are termed *hemihedral* or *half-sided*, since they are formed by the development of half the sides of the complete or *holohedral* form. Fig. 86 represents a combination of the tetrahedron (*o*) and cube (*a*). Fig. 87 the same, with the addition of the negative tetrahedron (*o*′). The most important of the remaining hemihedral forms of the regular system is the *pentagonal dodecahedron*, fig. 88, which is the hemihedral form of the four-faced cube, and hence has the symbol $\frac{\infty O m}{2}$.

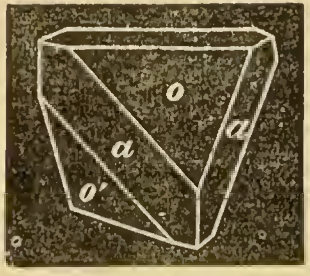

Fig. 86.

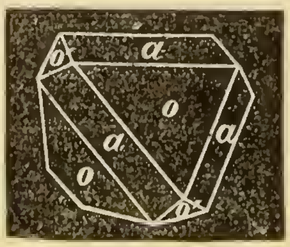

Fig. 87.

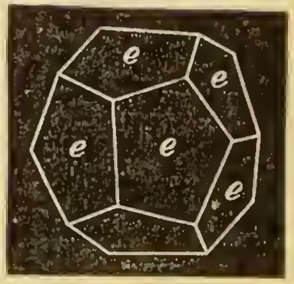

Fig. 88.

The tetrahedron is observed on sodium antimony sulphide (Schlippe's salt), sodium chlorate and bromate, silicon, diamond, cuprous chloride, zinc-blende, boracite, etc. The pentagonal dodecahedron is occasionally found on lead nitrate, and on sodium bromate and chlorate; it is especially frequent on iron pyrites and on fahl-ore.

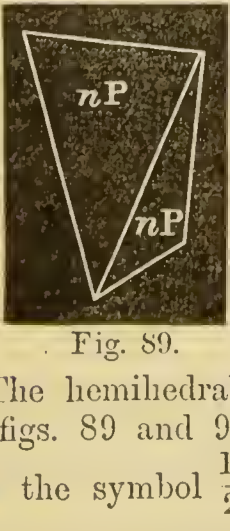

Fig. 89.

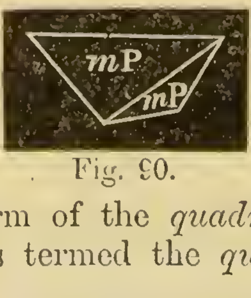

Fig. 90.

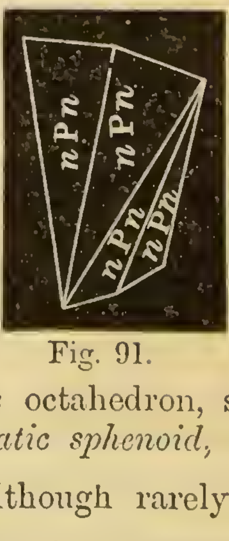

Fig. 91.

The hemihedral form of the *quadratic* octahedron, seen in figs. 89 and 90, is termed the *quadratic sphenoid*, and has the symbol $\frac{P}{2}$. It occurs alone, although rarely, on mercuric cyanide and on strontium formate; in combination with holohedral forms it is more common. The octagonal pyramid or *di-octahedron* in this system yields a hemihedral form; it is termed the scalenohedron, fig. 91.

By far the most important hemihedral forms are those belonging to the hexagonal system, and of these the most common is the *rhombohedron*, fig. 92. It is derived from the double six-sided pyramid by the development of one-half the faces to the exclusion of the other half, in the manner indicated by fig. 93. Fig. 94 represents a combination of the rhombohedrons R and 2R (the latter derived from 2P), with the hexagonal prism ∞P. Fig. 95 shows a combination of

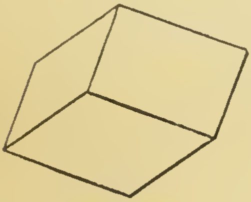
Fig. 92.

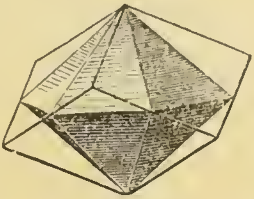
Fig. 93.

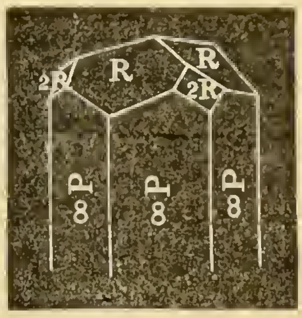

Fig. 94.

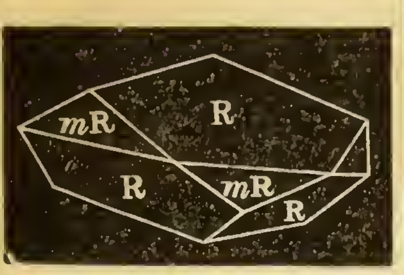

Fig. 95.

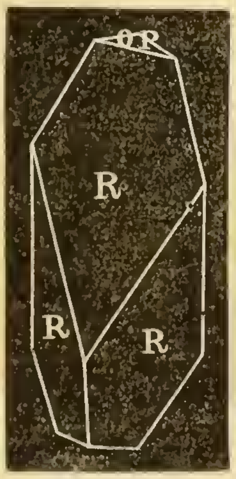

Fig. 96.

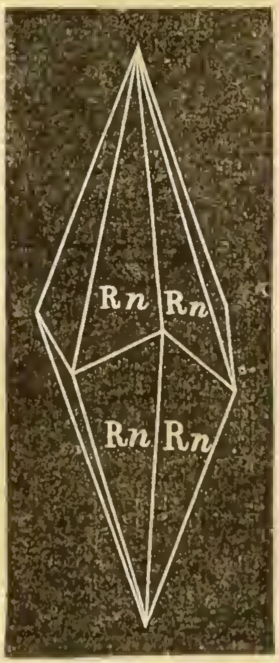

Fig. 97.

two rhombohedrons of different steepness, and fig. 96 a combination of an acute rhombohedron and the base. These forms are very common on calc spar, and on the naturally occurring carbonates of iron, manganese, magnesium, and zinc. Sodium nitrate possesses similar forms. The *scalenohedron*, fig. 97, is the hemihedral form of the dihexagonal pyramid. Occasionally, only half the faces of the scalenohedron are developed, and a form with only one-fourth the number of sides of the primary dihexagonal pyramid results; it is termed the *tetartohedron.*

The tetrahedron of the rhombic octahedron, termed the *rhombic sphenoid* $\frac{P}{2}$, is frequently observed in combination on magnesium and zinc sulphates. Fig. 98 represents a combination of the prism ∞P with $\frac{P}{2}$ occurring on these salts.

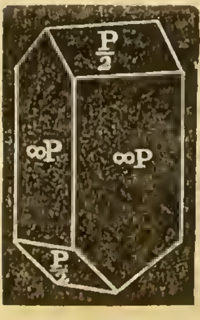

Fig. 98.

Twin Crystals. — Groups of crystals are occasionally met with which appear as if mutually intersecting one another; or as if one crystal had been divided in a direction parallel to one face, one-half turned round and then reunited. If we suppose that the octahedron, fig. 99, is divided parallel to one face, and one-half turned through 90°, we obtain the *hemitrope* seen in fig. 100, frequently observed on lead nitrate, alum, and magnetite. Such forms are termed *contact-twins* in contradistinction to *intersection-twins*, such as that of the cube, fig. 101, seen on ammonium chloride, and pyrites.

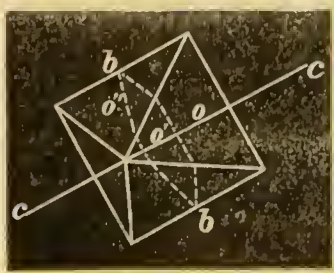

Fig. 99.

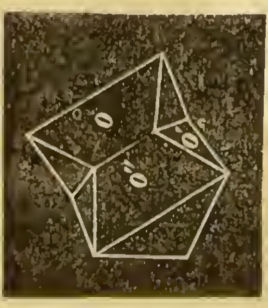

Fig. 100.

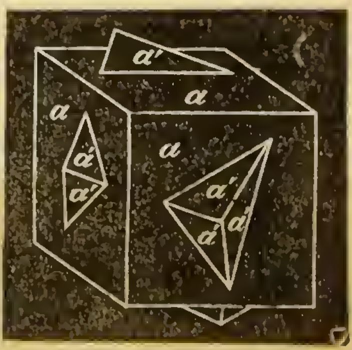

Fig. 101.

Twin crystals or *macles*, as they are sometimes termed, are observed on forms belonging to the whole of the systems. Fig. 102 represents a macled crystal of tin-stone (quadratic). Fig. 103 one of staurolite (rhombic), and fig. 104 of selenite (monoclinic). Twin crystals may usually be recognised by their re-entering angles.

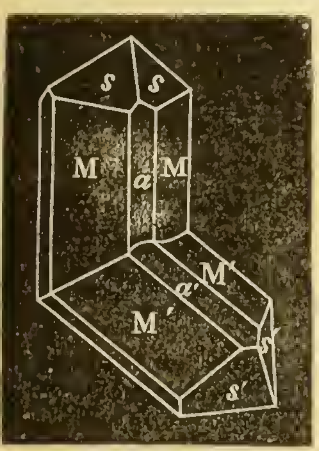

Fig. 102.

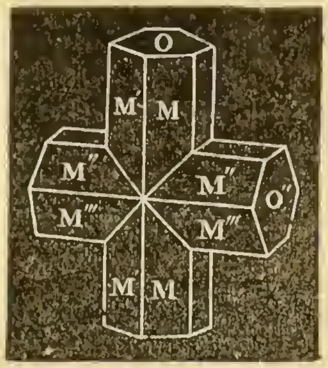

Fig. 103.

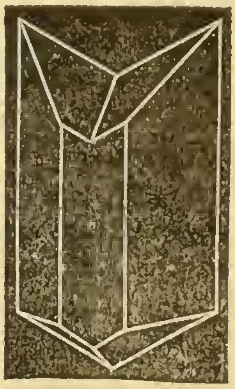

Fig. 104.

The complete description of the physical characters of a crystal includes the determination of its direction of least coherence, *i.e.*, the direction in which it is most readily split or cloven. The cleavage planes of a crystal are usually those of the simpler forms of the system to which it belongs, and often afford great assistance in the determination of its true crystallographic relations. The nature of the fracture and the structure (*i.e.*, whether fibrous, stellate, granular, etc.), are important characteristics, more particularly in natural crystals. The optical properties of crystals, especially their refractive and polarising powers, are of great importance in determining the particular system to which they belong.

CHAPTER IV.

THE METALS.

The 64 elementary bodies known to the chemist are divided into two groups of 49 metals and 15 non-metals. The majority of the metals are sparingly distributed, and some are met with only in rare minerals, and are of little practical importance; few of them occur in the free state, although some are never found in any other condition. With the exception of mercury they are all solids, and possess a characteristic *lustre* when in mass. Gold and silver are translucent in thin plates, but none of the other metals have been obtained in sufficiently thin leaves to allow of the transmission of light. When finely divided their power of reflecting light disappears, but on compressing their particles together it again becomes manifest. As a rule, the metals appear to possess a white or grey colour. Gold and the metals of the alkaline earths are yellow, copper is red, and bismuth and potassium have a pink tinge. It is to be observed, however, that the true colours of the metals are difficult of detection from the circumstance that the greater portion of the light which falls upon their surfaces is simply reflected without change; hence the tint due to the feeble decomposition of the light is greatly diluted, or even entirely masked, by the great proportion of this reflected white light. By repeatedly reflecting the light from surface to surface of the metal, the proportion of decomposed to ordinary light is gradually augmented, and the true colour of the metal becomes apparent. Starting from the fact that when white light is decomposed, the reflected coloured ray is complementary to the absorbed or transmitted ray, Seely has suggested that the natural colour of the alkali-metals is copper-red, since solutions of these metals in liquid ammonia appear blue by transmitted light, and to this colour copper-red is complementary.

The specific gravities of the various metals, so far as these are known, are contained in the following Table:—

Lithium,	0·578—0·589	Cadmium,	8·6
Potassium,	0·865	Molybdenum,	8·6
Sodium,	0·972—0·985	Nickel,	8·8—9·0
Rubidium,	1·52	Copper,	8·8—8·9
Calcium,	1·566—1·584	Bismuth,	9·8—9·9
Magnesium,	1·743	Silver,	10·4—10·53
Glucinum,	2·1	Lead,	11·3—11·4
Strontium,	2·50—2·58	Thallium,	11·8—11·9
Aluminium,	2·50—2·67	Rhodium,	11·0—11·2
Barium,	4·0	Ruthenium,	11·0—11·4
Zirconium,	4·15	Palladium,	11·3—11·8
Antimony,	6·72	Mercury,	13·596
Chromium,	6·8	Uranium,	18·4
Zinc,	6·9—7·0	Tungsten,	19·261
Tin,	7·3	Gold,	19·3—19·5
Indium,	7·2—7·4	Platinum,	21·5
Iron,	7·8—8·1	Iridium,	22·4
Cobalt,	8·5—8·9		

Many of these numbers must be considered as only approximately accurate on account of the difficulty of obtaining the metals in the pure state. Some of them, however, correspond to real differences in specific gravity depending upon particular conditions of the metal. As a rule, the specific gravity of the metals is increased by hammering and rolling; bismuth, however, forms an exception. The specific gravity of the metal as wire is usually less than that of the same metal rolled. Electrolytically-deposited metals also differ in specific gravity from the same metals reduced by heat. The following Table contains examples of these differences:—

Iron, wrought,	7·74—7·87	Thallium, cast,	11·853
,, wire,	7·6 —7·7	,, wire,	11·808
,, electrolytic,	8·139	Bismuth, crystallised,	9·935
Copper, rolled,	8·88—8·93	,, quickly cooled,	9·677
,, wire,	8·63—8·9	,, after pressure,	9·556
,, electrolytic,	8·94		

The metals manifest great variations in capacity of extension under the hammer, or between rollers. Some of them, like gold and silver, may be obtained in exceedingly thin leaves; others, like antimony and bismuth, appear to be perfectly immalleable. Similar differences are noticed in the tenacity of the metals; some of them can be drawn out into very fine wire; others are altogether destitute of ductility. The following Table, due to Wertheim, shows the weight in kilograms required to break different wires of 1 square millimetre in thickness:—

Lead,	2·2	Platinum,	34
Tin,	2·6	Copper,	40
Gold,	26	Iron,	63
Silver,	29	Cast-steel,	83

These numbers were obtained from carefully prepared and well annealed specimens; for results observed in actual practice, and on the large scale, in the case of the common metals, the student is referred to Anderson's *Strength of Materials* (Longmans).

Metals conduct heat and also electricity very unequally; the order of conductivity in both cases appears, however, to be the same:—

	CONDUCTIVITY.	
	Thermal.	Electric.
Silver,	100	100
Copper,	73·6	79.3
Zinc,	28·1	27·3
Tin,	14·8	17·0

The metals show great differences in fusibility and volatility; mercury is liquid, and emits vapour at ordinary temperatures; gallium softens between the fingers, and rubidium, potassium, and sodium melt below 100°. The following table shows the fusing and boiling points of a number of metals:—

	Melting Point. °C.	Boiling Point. °C.		Melting Point. °C.	Boiling Point. °C.
Mercury,	−39·4	357	Thallium,	294	...
Rubidium,	38·5	...	Cadmium,	320	860
Potassium,	62·5	...	Lead,	334	...
Sodium,	97·6	...	Zinc,	423	1040
Indium,	176	...	Silver,	1025	about.
Lithium,	180	...	Copper,	1200	
Tin,	235	...	Gold,	1200	
Bismuth,	268	...			

Many metals melt only at the very highest temperatures, and the determination of the exact point is a matter of great difficulty; certain of them soften before actual fusion occurs, so that they can be hammered or *welded* into compact masses.

COMPOUNDS OF METALS WITH METALS—ALLOYS.

The affinity of the metals for one another is comparatively feeble, and the combinations produced by their mutual union are generally unstable. In certain cases, as in the addition of the alkaline metals to mercury, or when copper is mixed with zinc, or tin with platinum or gold, heat is produced indicating the existence of a certain amount of chemical affinity; but as a rule, little or no thermal disturbance results from the admixture of melted metals. Certain alloys appear to be only capable of existence when fluid; on solidification, the constituent metals separate and arrange themselves in the order of their densities. Definite combinations of the metals are frequently difficult to obtain, since they appear to dissolve in all proportions in the excess of one or other of the constituents, and, generally speaking, the solidifying point of the alloy is so near that of one or other of the admixed metals that it is impossible to isolate the combination by any process of crystallization. In one or two cases, however, such a method is practicable, and is taken advantage of, as in the extraction of a silver-lead alloy in Pattinson's process for desilverising lead.

As a rule, the specific gravity of an alloy is different from that calculated from the relative weights of the constituents, on the assumption that no alteration of volume had occurred. Moreover, its melting point is generally lower than the mean melting point of the metals; this fact, however, is of small value as indicating the existence of chemical union, since the fusion point of a mixture of salts is generally lower than that of the most difficultly fusible of its ingredients, and is frequently different even from the calculated mean melting point. The solidifying point of an alloy is often much lower than its point of fusion. The colour, hardness, and tenacity of metals frequently change on alloying, and the behaviour of the alloys towards reagents is, in many cases, different from what we should expect from the nature of the constituent metals. Thus nitric acid has little or no action on platinum, although it rapidly dissolves silver; an alloy of the two metals is, however, readily dissolved by this acid. On the other hand, when silver is added to gold in certain proportions the alloy is unacted upon by nitric acid.

The special character of the alloys will be described in connection with one or other of their component metals.

COMBINATIONS OF THE METALS AND NON-METALS.

In alloys the peculiar lustre and general metallic character of the constituents are preserved; in combinations of the metals with the non-metals the characteristic properties either disappear or are very considerably modified.

7. **Metallic Hydrides.** — Comparatively few metallic hydrides are known, and the compounds which have actually been prepared are very unstable. Antimony forms a gaseous hydride of the composition SbH_3, analogous to the hydrides of nitrogen, phosphorus, and arsenic; it decomposes with great ease even at ordinary temperatures, and cannot be obtained unmixed with hydrogen. Hydrogen is absorbed or *occluded* by many metals, notably by palladium, with the formation in all probability of a definite alloy, Pd_4H_2. Favre has shown that the heat developed by the union is the same for the last as for the first portion of hydrogen added, which is not true in the case of the absorption of hydrogen by platinum, charcoal, etc., which are purely cases of capillary affinity, in which the gas may be assumed to form a layer, the density of which diminishes with the distance from the surface of the solid. Troost and Hautefeuille have described combinations of hydrogen with the alkaline metals. The best known hydride is that of copper; it is a reddish-brown powder which in contact with hydrochloric acid forms cuprous chloride and free hydrogen.

Zinc, iron, and magnesium also appear to form hydrides, but their composition is unknown.

8. **Metallic Oxides.**—All the metals unite with oxygen, and many of them in more than one proportion. The affinity which they manifest, however, for that element is very variable; some of them, like the metals of the alkalies and

alkaline earths, cannot be exposed to the air without immediate oxidation resulting, whereas the oxides of gold, silver, and platinum, ruthenium, rhodium, and iridium, can only be procured by indirect methods. Iron and lead, when massive, experience no change in dry air, but when very finely divided they are oxidised with incandescence. The oxides are generally prepared by heating the corresponding hydrates or the oxygen salts of volatile acids. As a rule, they are opaque, lustreless bodies, for the most part fusible, but not readily volatilised. Some of them are decomposed on heating, and the greater number may be reduced either to the metal or to a lower state of oxidation by ignition with carbon, hydrogen, or carbon monoxide. Chlorine usually converts the oxide on heating into a chloride or oxychloride; sulphur forms a sulphide with certain metals, especially with the so-called heavy metals, with others it produces a sulphate; on alumina, magnesia, and the oxides of tin, titanium, and chromium, it has no action.

9. Metallic Hydrates.—The oxides may be regarded as derived from one or more molecules of water by the replacement of the hydrogen by the metal: *e.g.*,

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \quad \left.\begin{matrix}K\\K\end{matrix}\right\}O \quad \overset{II}{Ca}\Big\}O \quad \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 \quad \overset{IV}{Sn}O_2 \quad \left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3 \quad \left.\begin{matrix}\overset{III}{In}\\\overset{III}{In}\end{matrix}\right\}O_3$$

By replacing only a moiety of the hydrogen the corresponding hydroxide results:

$$\left.\begin{matrix}K\\H\end{matrix}\right\}O \quad \left.\begin{matrix}\overset{II}{Ca}\\H_2\end{matrix}\right\}O_2 \quad \left.\begin{matrix}\overset{III}{In}\\H_3\end{matrix}\right\}O_3$$

The hydroxides are generally more or less soluble in water, and possess an alkaline reaction; even many of those which are usually accounted insoluble in water, as those of silver and zinc, yet dissolve in sufficient quantity to show this reaction. The majority of the hydroxides are decomposed on heating with the formation of water and the corresponding oxide; some of them, like aluminium hydroxide, require a very high temperature to effect the complete expulsion of the water; others, like potassium hydroxide, retain it, apparently, at all temperatures.

10. Metallic Chlorides.—All the metals combine with chlorine; and, as a rule, to which however there are many exceptions, each metallic oxide has a corresponding chloride. Many of the chlorides occur native, and constitute valuable minerals. They may be artificially prepared by the direct union of chlorine with the metal; or by the action of the gas upon the heated oxide, either alone or mixed with charcoal; or by the action of hydrochloric or nitro-hydrochloric acid upon the heated oxide, either alone or mixed with charcoal; chlorides may be obtained by the action of hydrochloric acid upon the sulphate. Some chlorides may be obtained by the action of a metallic chloride upon a metal; thus stannous chloride may be formed by heating a mixture of granulated tin and mercuric chloride:—

$$HgCl_2 + Sn = SnCl_2 + Hg.$$

The majority of the chlorides are soluble in water, and some of them dissolve in alcohol and ether. On the addition of a large volume of water to the solution of certain chlorides, *oxychlorides* are formed; *e.g.*, in the case of bismuth chloride:

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

Other chlorides, as, for example, those of antimony, vanadium, and titanium, are completely decomposed by water. Most of them are volatile at a sufficiently high temperature without decomposition; but not unfrequently the higher chlorides lose chlorine on heating. With the exception of the chlorides of the alkalies and alkaline earths, they are reduced on heating in hydrogen with production of the metal, or a lower chloride and hydrochloric acid. Some of them, like the chlorides of copper and silver, are reduced to the metallic state in contact with iron or zinc in dilute hydrochloric or sulphuric acid. Sulphuric acid, and also nitric acid, by repeated treatment, decompose the greater number of the chlorides at a gentle heat; at higher temperatures they are also decomposed by phosphoric and boric acids. Most of them evolve chlorine on treatment with manganese dioxide and sulphuric acid; and when heated with potassium dichromate and strong sulphuric acid, they form *chromyl dichloride* (CrO_2Cl_2), a dark-red volatile liquid decomposed by water, with formation of chromic and hydrochloric acids. Many chlorides exhibit a tendency to combine together forming so-called double salts, *e.g.*, $2KCl.PtCl_4$; $2NH_4Cl.PtCl_4$; $HgCl_2.2NH_4Cl$.

11. **Metallic Bromides.**—These compounds are similar to the corresponding chlorides, and for the most part may be obtained by analogous methods. They are, in general, fusible, and may be volatilised at a sufficiently high temperature. They are decomposed by chlorine or by hydrochloric acid, with elimination of bromine or production of hydrobromic acid. Heated with manganese dioxide and sulphuric acid, bromine is evolved, but no compound analogous to chromyl dichloride is formed on the addition of sulphuric acid and potassium dichromate.

12. **Metallic Iodides.**—The iodides are, in general, similar in composition and properties to the corresponding bromides and chlorides, and may be prepared by like methods. They are decomposed by bromine, or on heating with hydrobromic acid; they are fusible, but are usually less volatile than the bromides or chlorides. They are decomposed on heating with sulphuric acid, with formation of hydriodic acid, sulphur dioxide, and free iodine.

13. **Metallic Fluorides.**—A few fluorides are found native. Those which are known only as artificial preparations are not easily obtained pure, and are difficult to preserve. They may be obtained by dissolving the metals or their oxides, hydrates, or carbonates, in hydrofluoric acid; or by heating the metals with already formed metallic fluorides; thus, antimony fluoride may be obtained by heating that metal with lead or mercury fluoride. Certain fluorides, as for example those of arsenic, chromium, and titanium, can be prepared by heating the corresponding oxides with fluor-spar and Nordhausen acid or oil of vitriol: *e.g.*, $As_2O_3 + 3CaF_2 + 3SO_4H_2 = 2AsF_3 + 3CaSO_4 + 3H_2O$.

The fluorides, for the most part, resemble the corresponding chlorides, but, in general, they are much less soluble in water than those bodies. Silver fluoride, however, is readily dissolved; on the other hand, the fluorides of the alkalies and alkaline earths are but sparingly soluble. When dry, they may be ignited without decomposition; when heated with sulphuric acid they are converted into sulphates, with evolution of hydrofluoric acid.

The fluorides show a remarkable tendency to form double salts; the following are examples of such compounds:—

Ammonium hydrofluoride, ... $NH_4F.HF$
Potassium borofluoride, ... $KF.BF_3$
Potassium silicofluoride, ... $2KF.SiF_4$.

Analogous compounds of titanium, tin, and zirconium are also known.

14. Metallic Compounds of the Halogens and Oxygen.—The most important of these combinations are the chlorates and perchlorates, iodates and periodates; the corresponding bromine compounds are very unstable, and but little is known of them. The chlorates are formed by solution of the metal or its oxide, hydrate, or carbonate in chloric acid; or by the action of chlorine upon a hot solution of the hydrate; thus in the case of potassium chlorate—

$$6HKO + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

By keeping the solution cold during the action of the gas, *potassium hypochlorite* is obtained—

$$2KHO + Cl_2 = KClO + KCl + H_2O.$$

The chlorates may, indeed, be obtained from the hypochlorites by simply boiling their solutions—

$$3KClO = KClO_3 + 2KCl.$$

They may also be readily obtained by adding the corresponding sulphate to barium chlorate, *e.g.*—

$$Tl_2SO_4 + Ba(ClO_3)_2 = 2TlClO_3 + BaSO_4.$$

The only important hypochlorite is the calcium compound, the preparation of which has already been described (Vol. I., p. 274). All the chlorates are dissolved by water, the most sparingly soluble being the potassium and thallium salts. They are decomposed on heating, either with the evolution of oxygen and the formation of a metallic chloride, or with the evolution of both oxygen and chlorine, and the production of an oxide or oxychloride—

$$2KClO_3 = 2KCl + 3O_2$$
$$4Pb(ClO_3)_2 = 2(PbCl_2.PbO) + 2Cl_2 + 11O_2;$$
$$2Ni(ClO_3)_2 = 2NiO + 2Cl_2 + 5O_2$$

In the case of potassium chlorate, a certain amount of perchlorate is formed at an intermediate stage of the decomposition. The chlorates are decomposed by sulphuric acid, with formation of chlorine tetroxide (Vol. I., p. 277), by hydrochloric acid with the production of free chlorine, in addition to the tetroxide (*loc cit*), and by nitric acid with formation of nitrate, perchlorate, free oxygen, and chlorine.

The *perchlorates* are best formed by dissolving the metal or its oxide in perchloric acid, or by the action of a sulphate upon barium perchlorate: thus in the case of thallium perchlorate—

$$Tl_2SO_4 + Ba(ClO_4)_2 = 2TlClO_4 + BaSO_4.$$

Potassium perchlorate is readily obtained by the action of heat or nitric acid upon the chlorate; on treating the product with water, the more soluble chloride or nitrate is readily washed away, and the perchlorate may be purified by recrystallization. The perchlorates are more or less soluble in water, the potassium compound being one of the most insoluble. They are generally deliquescent, and may be heated to a higher temperature than the chlorates without decomposition; strong sulphuric acid liberates perchloric acid without evolution of chlorine.

The *iodates* are more numerous than the chlorates, on account of the tendency of iodic pentoxide to form acid or anhydro-iodates; thus no less than three potassium iodates are known, viz.—

Normal potassium iodate,..............	KIO_3
Potassium di-iodate, ...	$K_2I_4O_{11} = 2KIO_3.I_2O_5$
Potassium tri-iodate,....................	$KI_3O_8 = KIO_3.I_2O_5.$

The iodates may be formed by bringing iodine in contact with a hydroxide, and removing the iodide simultaneously formed by digestion with alcohol; or by the action of iodic acid upon the oxide or metal. They are, in general, but sparingly soluble in water, and are decomposed on heating in a similar manner to the chlorates. The basicity of iodic acid is not definitely established; there is reason to believe that it is bibasic, unlike chloric and bromic acids, which are monobasic; moreover, the iodates, with the exception of the barium salt, are not isomorphous with the corresponding chlorates; on this view the molecular formula of the acid would be $I_2O_6H_2$.

The constitution of *periodic acid* is still a matter of doubt; its salts appear to be best represented on the assumption that its molecule has the composition H_5IO_6; the following formulæ express the composition of a number of its derivatives:—

Di-sodium periodate,	$Na_2H_3IO_6$
Tri-potassic periodate,	$K_3H_2IO_6$
Mono-ammonium periodate,	$NH_4H_4IO_6$
Diargentic periodate,	$Ag_2H_3IO_6$
Penta-argentic periodate,	Ag_5IO_6
Lithium ammonium periodate,	$LiNH_4H_3IO_6$
Barium periodate,	$Ba_3H_4I_2O_{12}$.

The periodates are, in general, very sparingly soluble in water; they are decomposed on heating into a metallic iodide or into a mixture of iodide and oxide or metal and free oxygen.

15. Metallic Sulphides.—As a rule, for each oxide we have a corresponding sulphide, although instances to the contrary are by no means rare. Moreover, certain sulphides are known to which we have no analogous oxide. Many sulphides occur in nature, and constitute important sources of metals; thus lead, copper, zinc, mercury, and antimony, are largely extracted from their sulphides. The sulphides may be formed artificially (1) by the direct union of the metal and sulphur; or (2) by the action of sulphuretted hydrogen, or a solution of an alkaline sulphydrate on the metal, or on certain of its combinations, either in the dry state or in solution; or (3) by heating the oxide or sometimes the chloride in vapour of carbon bisulphide; or (4) by heating the sulphates with hydrogen, carbon, or organic matter.

The greater number of the sulphides are insoluble in water; when found native they are generally crystallised, sometimes in highly characteristic forms. They are usually of a dark colour, and are very rarely transparent. Lead sulphide, cinnabar, and realgar transmit light when in thin plates. Some of them are very soft, and many are easily fusible. Many of the lower sulphides suffer no change in composition on being heated out of contact with air; certain of the higher sulphides, however, part with a portion of their sulphur, and are converted into lower sulphides; a few sulphides, more especially those of gold and the platinum metals, are completely decomposed on heating.

All the sulphides, which are not completely decomposed by heat alone, suffer change in contact with heated air; sometimes an oxide of the metal is formed together with sulphur dioxide; sometimes a sulphate, and occasionally the metal itself is produced by the interaction of the oxidised products. Thus in the case of galena or lead sulphide, we have the following changes—

$$\begin{aligned}
&(1)\ PbS + O_3 &&= PbO + SO_2\\
&(2)\ PbS + O_4 &&= PbSO_4\\
&(3)\ PbS + 2PbO &&= Pb_3 + SO_2\\
&(4)\ PbS + PbSO_4 &&= Pb_2 + 2SO_2.
\end{aligned}$$

Reactions such as these are of great importance in many metallurgical operations. The nature of the change frequently depends upon the temperature of the oxidation; thus at low temperatures there is a tendency to the production of sulphates, whereas oxides are mainly formed by intense heating.

Certain metallic sulphides are decomposed by acids either in the cold or on heating; sulphuretted hydrogen being evolved and a metallic salt formed; thus with ferrous sulphide and sulphuric acid—

$$FeS + H_2SO_4 = H_2S + FeSO_4,$$

so also with antimony sulphide and hydrochloric acid—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Strong nitric acid produces sulphuric acid, or a metallic sulphate, and a lower oxide of nitrogen; if the nitric acid be not concentrated, more or less sulphur is simultaneously liberated. Nitrohydrochloric acid reacts in a similar manner, a sulphate or occasionally, as in the case of mercury, a chloride of the metal being formed.

Certain metallic sulphides, notably those of the alkalies, form *sulphydrates* or *hydrosulphides* in contact with sulphuretted hydrogen; thus in the case of potassium monosulphide—

$$K_2S + H_2S = 2KHS.$$

This reaction is precisely analogous to that which occurs on adding potassium monoxide to water, when potassium hydroxide is formed—

$$K_2O + H_2O = 2KHO.$$

On adding hydrochloric acid to potassium sulphydrate, sulphuretted hydrogen and potassium chloride are formed, exactly as water and potassium chloride are produced on the addition of hydrochloric acid to caustic potash—

$$KHS + HCl = KCl + H_2S$$
$$KHO + HCl = KCl + H_2O.$$

Many of the sulphides of the alkalies and alkaline earths are decomposed by water, with formation of a sulphydrate and hydroxide; thus barium sulphide decomposes into barium sulphydrate and barium hydrate—

$$2BaS + 2H_2O = BaH_2S_2 + BaH_2O_2.$$

The extent of the decomposition appears to depend upon the relative quantities of water and sulphide present; in strong aqueous solution, sodium sulphide ($Na_2S.9H_2O$) can exist unaltered. This is indicated by the fact that such a solution, when boiled with potassium ethyl-sulphate, yields principally ethyl-sulphide $(C_2H_5)_2S$, whereas it should yield mercaptan, C_2H_5HS, if the sulphide had been completely decomposed into the sulphydrate and hydroxide. By diluting the solution mercaptan is formed, in quantity depending upon the extent of the dilution.

The alkaline sulphydrates dissolve certain metallic sulphides forming so-called *sulphur-salts;* thus on adding arsenic trisulphide to ammonium or potassium sulphydrate, the *sulpharsenite* of ammonium or potassium is produced: arsenic pentasulphide also exists in combination with metallic sulphides, forming the so-called sulpharsenates. The general composition of these salts may be represented by the formulæ:

Metasulpharsenate,...................... $MAsS_3$
Pyrosulpharsenate, ... $M_4As_2S_7$
Orthosulpharsenate,...................... M_3AsS_4

corresponding to the meta-, pyro-, and ortho-modifications of phosphoric acid, or to the analogous *sulphophosphates.*

A series of unstable compounds, known as *sulphocarbonates*, are formed by the action of carbon bisulphide upon the hydroxides; thus with caustic potash—

$$6KHO + 3CS_2 = 2K_2CS_3 + K_2CO_3 + 3H_2O.$$

The sulphocarbonates of the alkalies and alkaline earths are yellow or red compounds, soluble in water; their solutions are gradually decomposed in the cold, but more quickly on heating, with the formation of a carbonate and sulphuretted hydrogen—

$$K_2CS_3 + 3H_2O = K_2CO_3 + 3H_2S.$$

Certain of these compounds have been extensively used in the treatment of vines against the ravages of phylloxera.

Selenium and tellurium also combine with the metals, forming combinations of analogous composition to the sulphides.

16. **Metallic Sulphites.**—Since sulphurous acid is dibasic, two series of sulphites are known, viz., *acid* and *normal sulphites*, analogous to the acid and normal carbonates, with which bodies, indeed, many of the sulphites are isomorphous. The alkaline sulphites are soluble in water; the sulphites of the alkaline earths are soluble in solutions of sulphurous acid; the sulphites of the heavy metals are for the most part insoluble in water. The soluble sulphites may be prepared by passing a current of sulphur dioxide into water containing the hydrate or carbonate, either in solution or suspension; the insoluble sulphites are best obtained by double decomposition. The salts are generally stable at ordinary temperatures when dry, but in solution they are gradually converted into sulphates; all acids, except boric and carbonic acids, decompose them with separation of sulphur dioxide. On heating to redness, they are decomposed into a metallic oxide and sulphur dioxide, or into a mixture of sulphate and sulphide. Nascent hydrogen converts them into metallic sulphides; hence with zinc and hydrochloric acid they evolve sulphuretted hydrogen. Acid sodium sulphite, or solution of calcium sulphite in sulphurous acid, are used as antiseptics, in the curing of fruit extracts, *e.g.*, lime-juice, or in arresting fermentation or putrefaction.

17. **Metallic Sulphates.**—The sulphates may be obtained (1) by the action of the acid upon the metal, its oxide, hydrate or carbonate; (2) by the action of sulphur trioxide upon the oxide, *e.g.*—

$$BaO + SO_3 = BaSO_4.$$

(3) By double decomposition—

$$BaCl_2 + Na_2SO_4 = 2NaCl + BaSO_4.$$

(4) By boiling an insoluble sulphate, with excess of an alkaline carbonate—

$$Na_2CO_3 + SrSO_4 = Na_2SO_4 + SrCO_3.$$

(5) By fusing an insoluble sulphate with a fixed alkaline carbonate—

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$

(6) By the oxidation of finely-divided sulphides, *e.g.*, in the weathering of pyritic shale—

$$FeS_2 + O_7 + H_2O = FeSO_4 + H_2SO_4.$$

The greater number of the sulphates may be obtained crystallised, and some of them are so found in large, well-developed forms. As a class, they are exceedingly stable salts, and many of them may be strongly heated without decomposition. They are generally dissolved by water; the sulphates of calcium, strontium, and lead are, however, sparingly soluble, and barium sulphate is almost insoluble in that liquid.

18. **Metallic Nitrides.**—Comparatively few combinations of nitrogen and the metals exist, and of several of those which are known the composition is still undetermined. Titanium, tungsten, uranium, chromium, copper, mercury, vanadium, and potassium form nitrides; these compounds are generally obtained by heating the metals in nitrogen, or their oxides or chlorides in ammonia. They are usually lustreless powders, of a black or brown colour; some of them are very readily decomposed, but others, as for example the nitrides of titanium and vanadium, may be intensely heated without change.

19. **Metallic Nitrites.**—These salts are, for the most part, soluble crystallisable bodies, generally either colourless or yellow; they may be heated to a moderate temperature without change, but at a red heat they are decomposed with evolution of nitrogen and oxygen, and formation of a metallic oxide. In solution they gradually become converted into nitrates, especially on heating, by absorption of oxygen. By long-continued boiling, solutions of the alkaline nitrites lose nitric oxide, and yield a nitrate and free alkali; thus in the case of potassium nitrite—

$$3KNO_2 + H_2O = KNO_3 + 2KHO + 2NO,$$

The nitrites may be prepared (1) by reducing the nitrates, either by ignition when they lose oxygen; or, as in the case of lead nitrite, by boiling the nitrate with the metal; (2) by the action of nitrogen tetroxide upon a hydrate—

$$N_2O_4 + 2KHO = KNO_3 + KNO_2 + H_2O.$$

On adding silver nitrate to the solution, the sparingly soluble silver nitrite is precipitated, from which the other nitrites may be obtained by the action of the chlorides of the respective metals.

20. Metallic Nitrates.—A few nitrates are found native, being formed by the action of the nitric acid, produced by the oxidation of organic or atmospheric nitrogen, upon bases contained in the soil. Potassium nitrate occurs as an incrustation upon the soil in several parts of the world, particularly in India; and sodium nitrate is found in beds of considerable thickness in certain parts of South America. The so-called *saltpetre-rot*, found upon the walls and floors of stables, cow-houses, and similar places, consists mainly of calcium nitrate; this salt and magnesium nitrate are frequently met with in greater or less quantity in well-waters. Nitrates also occur in the juices of plants; these salts are in all probability absorbed from the soil, and are not produced by the vital action of the plant.

The nitrates are, for the most part, readily soluble, neutral, crystalline salts; they fuse at comparatively low temperatures, and are decomposed by strong ignition. At moderate temperatures the nitrates of the alkalies and alkaline earths are mainly converted into nitrites, with evolution of oxygen; at still higher temperatures further decomposition ensues, oxygen, nitrogen, and nitrogen peroxide are evolved, and a basic oxide is left. The trisnitrates of bismuth and aluminium, which contain a large proportion of the acid-radicle, yield more or less nitric acid on heating, and form the trioxides of these metals. Silver nitrate yields metallic silver, but the nitrates of copper, mercury, lead, and, generally speaking, of those metals which form compounds with oxygen which are stable at moderately high temperatures, leave residues of the respective oxides. The ignition of the nitrate forms, indeed, in many cases, one of the readiest methods of procuring the oxide.

21. Metallic Phosphides.—The greater number of the metals appear to unite with phosphorus, but comparatively little is known of the composition and properties of the combinations. The phosphides of the alkalies and alkaline earths may be formed by heating their oxides with the vapour of phosphorus, and many of the insoluble phosphides may be produced by the action of hydrogen phosphide upon solutions of the several metals. These bodies are very prone to change; they absorb oxygen when moist, and some of them, in contact with water, evolve hydrogen phosphide and form a hypophosphite. A crystalline phosphide of iron, Fe_4P, has been prepared by Sidot; it is strongly magnetic and very hard. Hvoslef has described a phosphide of the composition Fe_6P, which, however, is not magnetic.

22. Hypophosphites and Phosphites.—The hypophosphites ($M\,PH_2O_2$, or $M''P_2H_4O_4$) are soluble crystalline salts, permanent when dry, but liable to oxidation in solution on exposure to air. They frequently inflame on heating, owing to the evolution of spontaneously inflammable hydrogen phosphide mixed with free hydrogen, and leave residues consisting of pyro- and meta-phosphates; thus with sodium hypophosphite—

$$5NaPH_2O_2 = Na_4P_2O_7 + NaPO_3 + 2H_3P + 2H_2.$$

Nickel and cobalt hypophosphites yield mixtures of metaphosphates and phosphides, and the phosphoretted hydrogen which they evolve is not self-inflammable—

$$3CoP_2H_4O_4 = 2CoP_2O_6 + CoP + H_3P + H_2.$$

The hypophosphites are best obtained by double decomposition from the barium salt and the sulphates of the several metals.

Barium hypophosphite, $Ba\,P_2H_4O_4.H_2O$, is prepared by warming phosphorus with baryta water, removing the excess of baryta by a current of carbonic acid, and crystallising by evaporation—

$$3BaH_2O_2 + P_8 + 6H_2O = 3BaP_2H_4O_4 + 2PH_3.$$

The hypophosphites have been mainly studied by Rose, Wurtz, and Rammelsberg. The thallium, calcium, cadmium, and lead salts are anhydrous; the sodium, lithium, barium, strontium, manganese, and uranium salts crystallise with one molecule of water; the magnesium, zinc, nickel, and cobalt salts with six molecules.

The hypophosphites in solution act as reducing agents, and give a white precipitate with silver nitrate, which rapidly darkens from the separation of silver.

The composition of the *phosphites* may be expressed under the general formulæ M_2PHO_3 or $M''PHO_3$ (neutral phosphites), and $MHPHO_3$, or $M''H_2P_2H_2O_6$ (acid phosphites). They are more stable than the hypophosphites, and are generally but sparingly soluble in water; they are decomposed on heating, yielding pyrophosphates (sometimes mixed with phosphites) and hydrogen, free from phosphoretted hydrogen. The soluble phosphites give white precipitates with calcium and barium chlorides; their solutions, when moderately dilute, give no precipitate with magnesium chloride in presence of ammonia and ammonium chloride.

23. Metallic Phosphates.—The general properties of the salts derived from the three modifications of phosphoric acid have already been described (Vol. I., p. 375, *et seq.*).

24. Metallic Carbides and Silicides.—The most important of these compounds are the silicides and carbides of iron; these bodies exert great influence in the preparation and on the properties of metallic iron. Certain varieties of "speigeleisen" have been supposed to consist mainly of a tetra-carbide of iron; a mono-, tri-, and octo-carbide have been described, but the proof of the definite existence of these bodies is not satisfactory.

25. Metallic Carbonates.—These salts cannot be readily formed by the direct union of carbon dioxide with a metallic oxide: thus, the dry gas has very little action upon perfectly dry lime. Moist carbon dioxide, *i.e.*, carbonic acid, acts immediately upon many oxides, even when only sparingly soluble in water, and certain metals, *e.g.* zinc and iron, yield carbonates when in contact with aqueous solutions of carbonic acid. A few basic radicles, *e.g.* aluminium, chromium, appear to be incapable of existing in union with carbonic acid. Many carbonates occur native, and constitute valuable ores and minerals. The carbonates of potassium, sodium, rubidium, cæsium, ammonium, and thallium are readily soluble in water; the lithium salt is but sparingly soluble, whilst the remaining carbonates are almost insoluble in water: the presence of carbonic acid in the solvent increases their solubility. On heating, the greater number of the carbonates of the heavy metals are decomposed; carbon dioxide is evolved and an oxide is formed. The carbonates of the alkaline earths require a much higher temperature, and the progress and extent of the decomposition are intimately connected with the tension of the carbon dioxide in the atmosphere surrounding them. Calcium carbonate begins to decompose at about 500°, but the quantity of gas evolved is very small, until the temperature exceeds 800°; if the carbon dioxide be prevented from escaping, the formation of gas proceeds slowly until its tension is equivalent to 85 mm. of mercury, when it stops, provided that the temperature remains constant: on raising the temperature to 1040° more gas is evolved, until its tension is equal to 520 mm., when the evolution again ceases. On removing the gas by means of a pump, a fresh quantity is evolved until the tension again reaches 520 mm. As the temperature is reduced, the carbon dioxide is slowly absorbed, the extent of the absorption varying with the diminution of heat. The state of equilibrium at any given temperature is attained when as many molecules of carbon dioxide combine with the lime as are expelled by the heat in the same time. If the carbon dioxide be removed as fast as it is liberated, so as to prevent its recombination with the lime, the calcium carbonate will be completely decomposed in time, even at a comparatively low temperature. The diminution of the tension of the carbon dioxide may be effected by diluting it with an indifferent gas, such as air, or hydrogen, or steam. Hence, by passing a current of such gas over the ignited carbonate, its decomposition is greatly facilitated.

The carbonates are decomposed by nearly all acids, with evolution of carbon dioxide; but silicic, boric, and a few of the acid-forming metallic oxides effect the decomposition only at a high temperature.

26. Metallic Silicates.—The greater portion of the earth's crust is composed of the silicates of aluminium, calcium, iron, magnesium, manganese, potassium, and sodium, existing to some extent as simple salts, but mainly as conjugated or double silicates. Comparatively few of the metals are found to form definite compounds with silica; this is especially true of the so-called heavy metals; certain of the simple silicates, and a few of the conjugated silicates, can be readily obtained artificially; indeed, some of them, as those of the alkalies, are only known as laboratory products. The naturally-occurring simple silicates may be included within the following limits of basic oxide and silica:—

$$\left.\begin{matrix}4M_2O\\ \text{or } 4\overset{II}{M}O\end{matrix}\right\}SiO_2 \quad \text{and} \quad \left.\begin{matrix}M_2O\\ \overset{II}{M}O\end{matrix}\right\}2SiO_2.$$

$$2M_2O_3.SiO_2 \quad \text{and} \quad M_2O_3.6SiO_2.$$

All silicates, with the exception of those of the alkalies, are insoluble in water; many of them are decomposed by nitric, hydrochloric, and sulphuric acids, with separation of pulverulent or gelatinous silica. They are all attacked by hydrofluoric acid, or ammonium fluoride, or by a mixture of fluor-spar and sulphuric acid, with formation of silicon fluoride. Fusion with alkaline carbonates or with microcosmic salt effects the decomposition of the insoluble silicates; in the former case an alkaline silicate is formed; in the latter the silica is set free, and floats in the fluid mass.

CHAPTER V.

GROUP I.—MONAD METALS.

LITHIUM.
SODIUM.
POTASSIUM.
RUBIDIUM.
CÆSIUM.
[AMMONIUM].

SILVER.

THALLIUM.

The metals of this group replace hydrogen in hydrochloric acid atom for atom, to form neutral chlorides of the general formula M′Cl., and of an atomic heat 12·6. The metals of the alkalies, lithium, sodium, potassium, rubidium, and cæsium, are soft, readily fusible, volatile bodies; they are easily oxidised on exposure to air, and decompose water at ordinary temperatures, with liberation of hydrogen and formation of hydroxides. They form soluble chlorides, sulphides, sulphates, carbonates, and silicates. Their atomic weights exhibit certain remarkable numerical relations: thus, the atomic weight of sodium is the arithmetic mean of the atomic weights of lithium and potassium: $\frac{7+39}{2} = 23$; and the atomic weight of rubidium is very nearly equal to the arithmetic mean of the atomic weights of potassium and cæsium: $\frac{39+133}{2} = 86$.

From the general similarity of the ammoniacal salts to those of the alkaline metals, it is convenient to study them in connection with this sub-group.

Silver forms an insoluble chloride, sulphide, phosphate, and carbonate; its oxide is very sparingly soluble in water. In its general characters and relations silver resembles sodium more than any other metal of the group of the alkalies.

In certain of its compounds thallium behaves as a triad: thus it forms a trichloride, $TlCl_3$, and a tri-sulphate $Tl_2(SO_4)_3$; on the other hand it is related to potassium and ammonium by the sparing solubility of the thallous platino-chloride and acid-tartrate. Moreover, a number of thallium, potassium, and ammonium salts have identical specific volumes; thus,

	Spec. vol.		Spec. vol.
KNO_3	47·9	$TlNO_3$	47·9
$KClO_3$	52·5	$TlClO_3$	52·2
K_2CO_3	65·6	Tl_2CO_3	65·2
AmCl	34·8	TlCl	34·2
AmH_2PO_4	65·0	TlH_2PO_4	63·7
Am_2SO_4	74·9	Tl_2SO_4	75·5
$AmHC_2O_4H_2O$	80·1	$TlHC_2O_4.H_2O$	78·0
$AmHC_4H_4O_6$	99·4	$TlHC_4H_4O_6$	100·7

These salts are isomorphous as well as isometric.

27. Lithium—Symbol Li.; atomic weight 7.—Lithium monoxide was discovered in 1817 by Arfvedson, in a naturally occurring silicate of aluminium and lithium, termed *petalite.* It is a very widely-diffused element, being found in many micas, in felspar, in the ashes of many plants, and in sea-water; it has also been detected in certain meteorites. The metal may be obtained by the electrolysis of the fused chloride. It has the colour and lustre of silver, it is soft and weldable, melts at 180°, and has a specific gravity of 0·58. It is the lightest solid known, being lighter even than any known liquid. When strongly heated, it burns with a white flame, forming the **monoxide,** and it is oxidised by water, without inflammation of the evolved hydrogen, forming **lithium hydroxide,** LiHO. This substance resembles the corresponding potassium and sodium compounds in its action on vegetable colours, and in its caustic taste. It is, however, less soluble in water than these compounds, and may be obtained in well-developed prisms by evaporation.

28. **Lithium Chloride,** LiCl, resembles common salt in appearance; it is, however, more deliquescent, is readily soluble in alcohol, and is partially decomposed on heating; it crystallises in cubes and in octahedrons, and may be obtained combined with two molecules of water by evaporation at a low temperature. It is found in many mineral springs: the Wheal Clifford spring in Cornwall forms, in fact, one of the most abundant sources of the element.

29. **Lithium Sulphate,** $Li_2SO_4.H_2O$, is obtained by the action of sulphuric acid on the chloride or the carbonate; it is a readily-soluble neutral salt, crystallising in prisms. It appears not to form an alum with aluminium sulphate. The **carbonate,** Li_2CO_3, and **phosphate,** Li_3PO_4, are sparingly soluble salts. The former may be obtained by adding ammonium carbonate to lithium chloride. It fuses at a red heat, and is partially decomposed. The phosphate is formed by adding a mixture of sodium phosphate and caustic soda to a soluble salt of lithium; it is almost insoluble in alkaline solutions, and is the form in which lithium is usually estimated quantitatively.

Lithium may be readily detected by the crimson colour which its salts impart to flame; on examining this light by means of the spectroscope, it is found to give a red band, Liα, between the Fraunhofer lines B and C, and an orange band, Liβ, between C and D.

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30. Sodium—Symbol Na; atomic weight 23·0.—In a state of combination sodium is one of the most abundant of the elements. Combined with chlorine, it is found as rock-salt, forming extensive deposits in many parts of the world: the chloride is also found largely in sea-water, and, to a greater or less extent, in nearly all spring-waters. The sulphate, nitrate, borate, and carbonate, also occur naturally, and the silicate enters into the composition of many rocks and minerals. Salts of sodium exist in nearly all organisms, vegetable and animal; and spectral analysis shows that this element is present in the atmospheres of the sun and fixed stars.

Sodium was first obtained by Davy by the electrolysis of the hydrate, and Gay-Lussac and Thenard showed that the metal might be obtained by the decomposition of the hydroxide exactly as in the case of potassium (*q.v.*). Sodium is now obtained on the large scale by heating the carbonate with charcoal and chalk in iron retorts or cylinders, as in the preparation of potassium. The process is much easier of execution, and yields a larger amount of metal than in the case of potassium, owing to the non-formation of secondary products.

Sodium has a specific gravity of 0·972; it may be readily cut with a knife at ordinary temperatures, but becomes hard and brittle when exposed to great cold. It melts at 97·6°; and may be volatilised; its vapour is dark blue. When exposed to the air it rapidly oxidises, and when strongly heated, it inflames and burns with a bright yellow light. It decomposes water with great rapidity, but the temperature of the decomposition is not usually sufficiently high to ignite the hydrogen. If, however, the water be heated, or if some mucilaginous substance be added to it, the hydrogen takes fire and burns with a yellow flame, from the presence of a trace of volatilised metal in the gas. The action of the metal on water may be thus represented—

$$Na + H_2O = NaHO + H.$$

Sodium absorbs hydrogen when melted, to form a **hydride** of the composition Na_2H. It is a silver-white body, of specific gravity 0·959, softer than the corresponding potassium compound, and less alterable in air. Sodium unites with oxygen in two proportions to form a monoxide, Na_2O, and a dioxide, Na_2O_2. The **monoxide** is a grey fusible powder, formed by heating the metal in dry oxygen or with the hydrate. The **dioxide** is obtained by the prolonged action of oxygen upon the monoxide. It is a white friable mass temporarily changing to yellow when heated; it dissolves in cold water without change, and the solution yields crystals of the composition $Na_2O_2.8H_2O$; with carbon monoxide it forms sodium carbonate; with nitric oxide, sodium nitrite; and with iodine, an oxyiodide, Na_2I_2O or $NaI.NaIO$.

31. **Sodium Hydrate,** or **caustic soda,** $NaHO$, may be obtained by the action of the metal upon water; in this way a very pure product may be prepared. It may also be made by decomposing moderately dilute solutions of the carbonate by milk of lime, and concentrating the clear caustic liquid in iron or silver vessels until it solidifies on cooling.

On the large scale the solution obtained by lixiviating "black ash," (see p. 110) is diluted to a specific gravity of about 1·1, and is mixed with burnt lime, in the proportion of about 15 cwt. of lime to a ton of caustic soda. Steam is blown through the mixture, when the following change occurs:

$$Na_2CO_3 + CaH_2O_2 = 2NaHO + CaCO_3.$$

The liquid is allowed to stand until clear, when it is run off from the sediment of calcium carbonate, and boiled down in shallow iron pans; undecomposed sodium salts (chloride, sulphate, carbonate, etc.) separate out and are removed by perforated ladles, and worked up again with fresh "salt-cake" in the "black ash" process, together with the sediment of calcium carbonate. When sufficiently concentrated, the strongly caustic liquor is heated in cast-iron pots until it becomes viscid. It is whitened by blowing air into it, or by the addition of sodium nitrate which decomposes the sulphides, cyanides, etc., by which it is coloured. The nitrate is decomposed with effervescence, and a quantity of graphite rises to the surface and is skimmed off. The melted mass is run into drums in which it solidifies. Commercial caustic soda is never chemically pure; in addition to more or less water, it contains varying amounts of silica, alumina, chlorides, sulphates, etc. It is largely used in the manufacture of soap and water-glass, in paper and starch making, in the refining of paraffin oils, etc.

Soda is less deliquescent than potash; it rapidly absorbs carbon dioxide from the air, and acquires a coating of the carbonate. It fuses below a red heat, and may be volatilised unchanged. It dissolves in water with great rise of temperature; a concentrated solution has a specific gravity of 1·5. A solution of specific gravity 1·385 when cooled, deposits colourless monoclinic (rhombic: Hermes) crystals melting at 6°, and of the composition $2NaHO.7H_2O$. Advantage might be taken of the separation of these crystals at low temperatures to purify sodium hydrate.

32. Sodium Chloride, or **common salt**, NaCl, has been known in all ages. Immense deposits of it occur in various parts of the world. The Cheshire beds are the principal sources of salt in this country; they were discovered towards the end of the 17th century, although the brine springs, which are also abundant in that district, have been worked from very early times. The largest salt mines in the world are at Wieliczka, in Galicia, and belong to the Austrian Government. At Cordova, in Spain, rock-salt is obtained by quarrying into a hill of the mineral. Large quantities of salt are obtained also from the steppes of Russia, and from the wastes of Persia, on the soil of which it occurs as an efflorescence.

In this country table-salt is chiefly obtained by the evaporation of brine springs in large shallow pans made of boiler-plate; if the evaporation is conducted rapidly, a fine-grained salt is formed: if conducted slowly, the large-grained flaky product used for salting fish, etc., is obtained.

In Germany, where the springs are usually much more dilute than those worked in this country, the evaporation is in part conducted by the action of the wind. The water of the spring is allowed to trickle over a stack of faggots or twigs freely exposed to the air (fig. 105). After having passed over the brushwood several times, the solution is sufficiently concentrated to be boiled down in pans.

Considerable quantities of salt are obtained on the coasts of Spain, Portugal, and France by the concentration of sea-water in shallow pits or troughs ranged along the shore. The sea-water is allowed to flow into a reservoir, where it deposits any suspended matter; afterwards it is run into smaller basins, where it is allowed to stand until the salt is crystallised out.

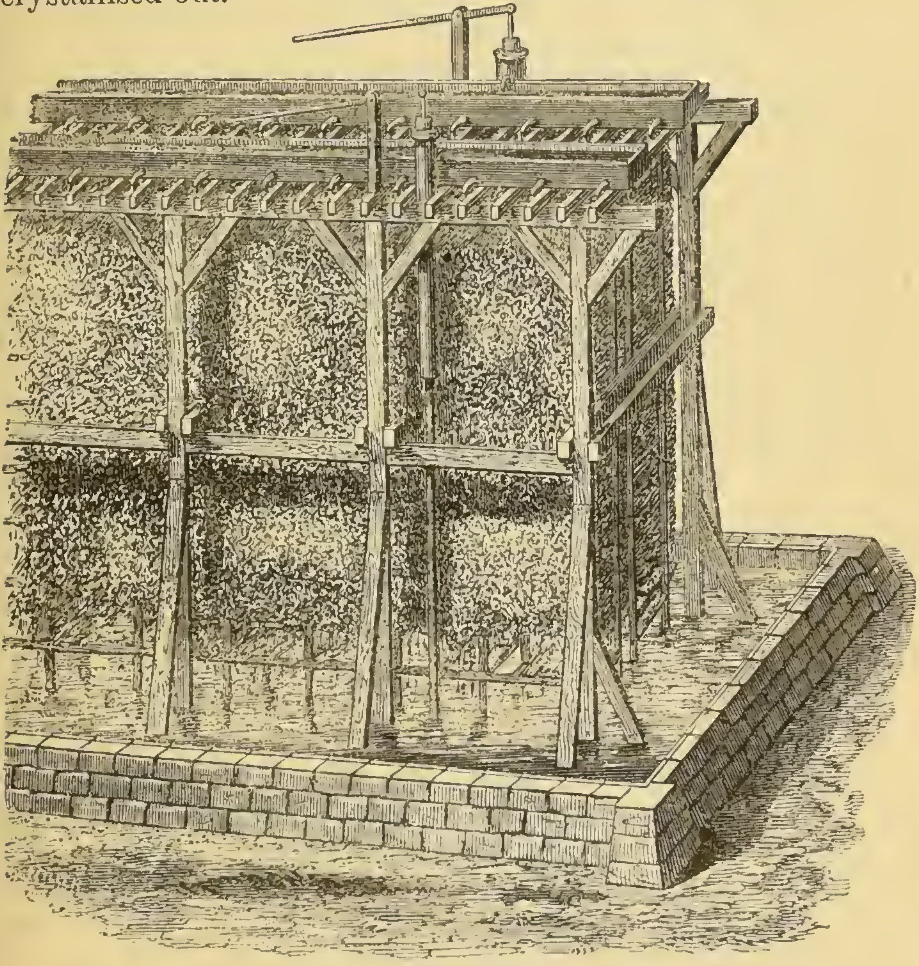

Fig. 105.

In Northern Russia and in Siberia, sea-water is concentrated by freezing, the ice which separates out containing only a relatively small proportion of salt-crystals; the residual brine on being boiled down yields common salt, frequently mixed, however, with considerable quantities of sodium sulphate and other salts.

Sodium chloride usually crystallises in colourless transparent anhydrous cubes, frequently grouped together in the curious manner seen in fig. 106; occasionally it is obtained in octahedrons and in other forms belonging to the regular system. When strongly cooled, its solution yields monoclinic crystals of the composition $NaCl.2H_2O$; at ordinary temperatures the crystals part with their water and break up into minute cubes. Sodium chloride is soluble in about three parts of cold water; its solubility increases very slightly with rise of temperature. On the addition of hydrochloric acid to its solution, it is precipitated. It is almost insoluble in strong alcohol. When suddenly heated, salt decrepitates, owing to the forcible expulsion of mechanically retained water: it fuses at 776°, and at a still higher temperature volatilises.

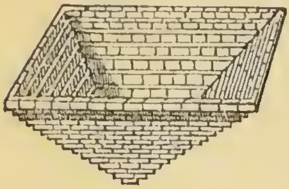

Fig. 106.

Salt is extensively used in the arts. It is the chief source of sodium compounds, and is used for glazing earthenware, and to some extent as a manure. It is an essential constituent of the food of man and of other animals. It is calculated that the annual consumption of salt as a condiment in this country amounts to about 20 lbs. for each person. **Sodium bromide, iodide,** and **sulphide** are analogous to the corresponding potassium salts (*q.v.*).

33. **Monosodium Hydrogen Sulphite,** $NaHSO_3$, may be obtained crystallised by saturating a solution of sodium carbonate with sulphurous acid. On adding as much soda to the liquid as it already contains, the disodium salt, Na_2SO_3, is obtained. By evaporation it may be obtained in monoclinic crystals containing seven molecules of water.

34. **Disodium Sulphate,** Na_2SO_4, was discovered by Glauber in 1658; hence its common name of "Glauber's salts." It is found native, as the mineral *Thenardite*, in Peru and in various parts of Spain. In union with calcium sulphate, it forms *Glauberite*, a mineral found in Spain and Austria. Di-sodium sulphate usually crystallises with 10 molecules of water in monoclinic prisms, which rapidly effloresce on exposure to air: they melt at 35°, and become completely dehydrated at 100°: the anhydrous salt melts

at 865°. A heptahydrated salt is known which crystallises in rhombic prisms. Disodium sulphate is most soluble in water at 34°. The maximum degree of solubility at this point is due to the fact that the salt dissolves as $Na_2SO_4.10H_2O$, the solubility of which increases with the temperature: beyond 34° it is changed into the anhydrous salt, the solubility of which gradually diminishes with the rise of temperature.

If a hot concentrated solution of the salt be allowed to cool slowly in a corked flask, it may be kept liquid for many weeks, but on touching it with a glass rod, or on throwing a fragment of the salt into it, it rapidly crystallises with the evolution of considerable heat (see Vol. I., p. 110).

Disodium sulphate dissolves in hydrochloric acid with loss of heat: the solution affords a convenient freezing mixture.

35. **Monosodium Hydrogen Sulphate**, $NaHSO_4$, is formed by the action, at moderate temperatures, of sulphuric acid upon common salt. It may also be obtained in transparent triclinic crystals by dissolving the preceding salt in dilute sulphuric acid. If strong sulphuric acid be poured over the dehydrated disodium salt, and the mass be heated, the **anhydro sulphate**, $Na_2S_2O_7$, is formed; it fuses at a red heat, evolves sulphur trioxide, and is converted into the disodium sulphate.

36. **Sodium Nitrate, Chili Saltpetre, Cubic Nitre**, $NaNO_3$, is found native in regular beds in the districts of Atacama, in Bolivia, and Tarapaca in Peru. It is used in this country as a manure, and for the manufacture of nitric acid and potassium nitrate. As it is slightly deliquescent, it cannot well be substituted for nitre in gunpowder. It crystallises in rhombohedrons, which are so obtuse as to give the crystals the appearance of cubes. It melts at 330°. It requires rather more than its own weight of water for solution: on dissolving it produces a considerable degree of cold. A solution saturated at 0° may be cooled to $-15{\cdot}7°$ before crystallization occurs; at this temperature laminated plates are formed, consisting of $NaNO_3.7H_2O$.

37. **Sodium Phosphates.**—The most important of these salts is the **disodium hydrogen phosphate** or **disodium**

orthophosphate, Na_2HPO_4, which is prepared by the addition of sodium carbonate to the solution of acid calcium phosphate obtained by treating bone-ash with sulphuric acid (Vol. I., p. 362). The solution is concentrated until the sodium phosphate commences to separate out and the crystals are purified by successive crystallizations. The crystals have usually the composition $Na_2HPO_4.12H_2O$, but by maintaining the solution at about 35°, the salt is obtained with only seven molecules of water. The 12-hydrated salt melts in its water of crystallization at 35° : it effloresces when exposed to air, and is converted into the 7-hydrated salt. The salt containing 12 molecules of water dissolves in about four parts of cold water : the solution has an alkaline reaction and a bitter taste. By the addition of caustic soda to the liquid, **trisodium orthophosphate**, $Na_3PO_4.12H_2O$, is formed crystallising in six-sided prisms. Its solution is strongly alkaline, and absorbs carbon dioxide, by which it is decomposed. By adding phosphoric acid to a solution of the ordinary phosphate, the **monosodium di-hydrogen phosphate**, $NaH_2PO_4.H_2O$, is formed. This salt may indeed be formed by the prolonged action of carbon dioxide upon a dilute solution of the ordinary phosphate. Its solution is strongly acid. On igniting the salt it is converted into **sodium metaphosphate**, $NaPO_3$, which fuses at a low red heat and solidifies to a glassy substance, highly deliquescent and readily soluble in water.

38. **Sodium Ammonium Hydrogen Phosphate** or **Microcosmic Salt**, $Na(NH_4)HPO_4.4H_2O$, is formed in putrid urine, and occurs in guano. It may be obtained artificially by dissolving six parts of the ordinary sodium phosphate in two parts of boiling water, and adding one part of ammonium chloride: common salt is precipitated, and microcosmic salt remains in solution—

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl.$$

On concentration it is deposited in monoclinic prisms. When heated, it loses water, hydrogen, and ammonia, and is converted into sodium metaphosphate; this salt constitutes a valuable flux in blowpipe operations.

39. **Sodium Pyrophosphate**, $Na_4P_2O_7.10H_2O$, is obtained by igniting ordinary sodium phosphate, dissolving the mass

in water, and concentrating the liquid when the salt crystallises out in monoclinic prisms. On boiling its solution with a dilute acid, it is reconverted into the ordinary sodium phosphate.

40. **Disodium Carbonate**, Na_2CO_3, is occasionally found native as an efflorescence on the soil; it exists in the soda lakes of Hungary, Egypt, and America, and in the water of the Geysers in Iceland. It is frequently met with on the surface of walls, being produced from the sodium salts contained in the plaster or mortar. The sodium carbonate of commerce was formerly entirely extracted from sea-weeds and from plants growing near the sea-shore. The dried plants were burned, and their ashes lixiviated, and the solution evaporated to dryness. The sodium carbonate thus obtained came into commerce under the name of *barilla;* it is still made to a small extent on the Spanish coasts. By far the greater portion of sodium carbonate which is now used in the arts is made from common salt by a process which is usually stated to have been invented by Leblanc. It consists in converting common salt into sodium sulphate by the action of sulphuric acid, and roasting the sulphate with ground coal and chalk, or limestone. The common salt is placed in the iron pan (fig. 107), and the requisite quantity of sulphuric

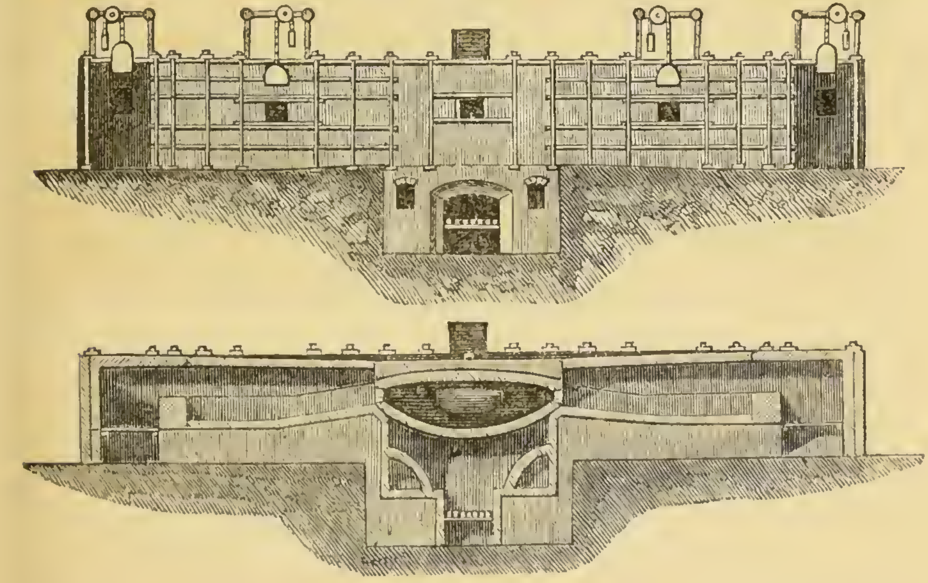
Fig. 107.

acid (chamber vitriol) is run in upon it. Hydrochloric acid escapes, and sodium hydrogen sulphate is formed—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The mass of undecomposed salt and acid sulphate is then raked on to the hearths of the furnaces at the side of the pan, where the mixture is more strongly heated, and the decomposition is completed in accordance with the equation—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The sodium sulphate, technically known as *salt-cake*, is roughly powdered, mixed with ground coal and limestone, and the mixture is heated to fusion on the hearth of a reverberatory furnace (fig. 108), when the following decomposition ensues:—

$$Na_2SO_4 + CaCO_3 + 4C = Na_2CO_3 + CaS + 4CO.$$

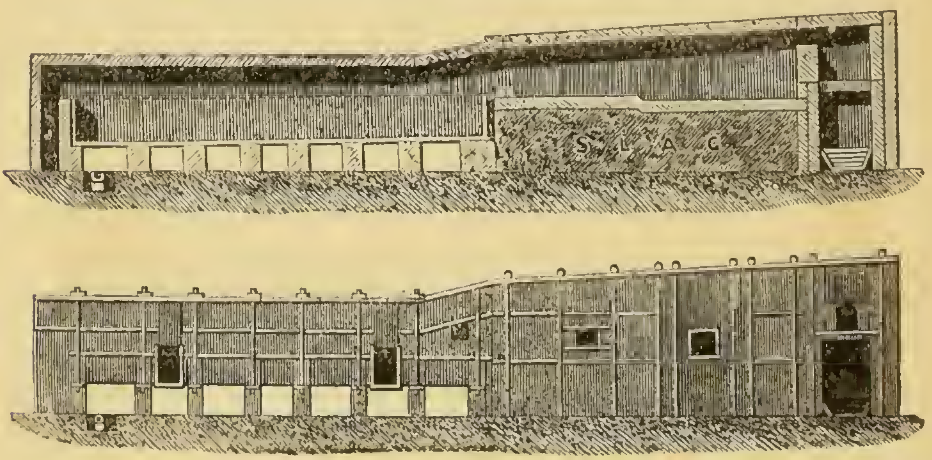

Fig. 108.

The fused mixture is raked into iron barrows, where it solidifies, forming what is known as *black ash*. When cold, the mass is broken up, thrown into tanks, and treated with tepid water. The sodium carbonate dissolves, and the calcium sulphide, in union with the salts of lime, together with a certain amount of combined soda (the quantity of which increases with the proportion of lime), remains undissolved. The tank-liquor evaporated to dryness, yields *soda-salt*, which, when calcined, forms the *soda-ash* of commerce. Soda-ash usually contains about half its weight of Na_2O, existing mainly as carbonate; it generally contains more or less hydrate, thiosulphate and cyanide, together with sulphate and chloride arising from imperfect decomposition. The sulphur indirectly employed to convert common salt into sodium carbonate remains almost entirely in the insoluble sediment known as *vat-* or *soda-waste.* Various processes have been proposed for its recovery; of these the most successful consists in blowing air through the mass of the waste for 12 or 15 hours, heating it with water, and mixing the solution with hydrochloric acid, and heating to about 60° with constant agitation, until the liquid smells of sulphur dioxide. Sulphur separates out, and collects upon the bottom of the decomposing vat. Calcium sulphydrate and bisulphide are first formed by the oxidising action of the air, and are afterwards converted into calcium thiosulphate, a portion of which is changed into calcium sulphydrate and insoluble calcium sulphite. On the addition of hydrochloric acid, calcium trithionate and small quantities of pentathionate are formed, together with sulphur and calcium chloride—

$$5CaS_2O_3 + 6HCl = 3CaCl_2 + 2CaS_3O_6 + 4S + 3H_2O.$$

On heating, the trithionate is decomposed into calcium sulphate, sulphur, and sulphur dioxide; the dioxide reacts upon a second portion of the thiosulphate, forming calcium trithionate and sulphur—

$$2CaS_2O_3 + 3SO_2 = 2CaS_3O_6 + S.$$

Various modifications of the original plan of Leblanc have been proposed with more or less success: thus it is found that the salt-cake may be obtained by treating the common salt, heated to low redness, with a mixture of air, sulphur dioxide (obtained direct from the pyrites burners), and steam. The use of sulphuric acid is thus obviated.

Sodium carbonate may also be obtained by passing ammonia and carbon dioxide gas into a solution of common salt; ammonium chloride and acid sodium carbonate are thus obtained:

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

The acid carbonate is converted into the normal salt by heating, and the ammonia is recovered from the solution by the addition of lime.

Dry sodium carbonate dissolves in water with evolution of heat, and the solution, which has an alkaline reaction and taste, yields crystals, the degree of hydration of which depends on the temperature of crystallization. The *soda-crystals* or *washing-soda* of commerce consists of the decahydrated salt $Na_2CO_3.10H_2O$: the crystals belong to the monoclinic system (fig. 109). They gradually effloresce on exposure to dry air, forming a white powder containing five molecules of water; in a vacuum the salt ultimately acquires the composition $Na_2CO_3.H_2O$. The mono- and deca-hydrate are found native, and are known respectively as *thermonatrite* and *natron*. Hydrates containing 15, 9, 8, 7, and 6 molecules of water have also been obtained. The salt containing 7 molecules of water appears to be dimorphous. The 10-hydrated salt requires about 7 parts of water for solution at 10°, and about 2 parts at 38°, at which temperature it is most soluble. The anhydrous salt fuses at 818°, and is perfectly unchanged when melted in dry air.

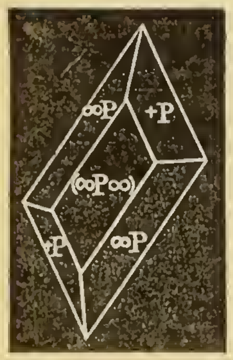

Fig. 109.

41. **Monosodium Carbonate,** or **Sodium Hydrogen Carbonate,** $NaHCO_3$, the *bicarbonate of soda* of commerce, is prepared on the large scale by exposing soda crystals to a stream of carbon dioxide. It is thus obtained as a crystalline powder, which, on solution, yields monoclinic crystals of considerable size. The solution, on boiling, evolves carbon dioxide, and is slowly converted into the normal salt. On heating the dry salt to a low red heat it also forms the disodium carbonate.

42. A **Tetrasodium Carbonate,** or **Sodium Sesquicarbonate,** $Na_4H_2C_3O_9.2H_2O$, is found native in Africa, in monoclinic crystals, and is known as *trona;* it may be regarded as a combination of the mono- and di-sodium carbonates, $2NaHCO_3 + Na_2CO_3$.

On mixing solutions of the normal potassium and sodium carbonates together, in equivalent proportions, monoclinic crystals of the composition $KNaCO_3.6H_2O$ are obtained. This so-called double salt has a lower fusing point than either of its constituents.

43. **Sodium Silicates.**—The simple alkaline silicates are

remarkable as being the only soluble silicates known; they are not found in nature, except, possibly, in solution in certain mineral waters. They occur in union with other silicates, notably those of ferric oxide and alumina, as in *felspar* and in the *micas;* comparatively few combinations of alkaline silicates with silicates of protoxides have been discovered; one of the best known is *pectolite,* $\left.\begin{matrix}\overset{\text{IV}}{\text{Si}}_3\\ \text{NaHCa}_2\end{matrix}\right\}O_9$. The sodium silicates derive their chief importance from their use as cements, and for hardening and preserving stone, and in mural painting. Water-glass, as the product is termed, is prepared by fusing sodium carbonate with twice its weight of quartz, and a small quantity of charcoal which is added to facilitate the decomposition of the carbonate, and to reduce any sulphates which may be present. Indeed, by the use of larger quantities of charcoal, water-glass may be prepared directly from the sulphate, the proportions being 5 parts of quartz, 3 parts of sodium sulphate, and 1 part of charcoal. The fused mass is pulverised and treated with boiling water, and the solution concentrated. Sodium silicate may also be obtained by heating powdered flints or sand with solution of caustic soda under a pressure of about four or five atmospheres. The product, in all cases, is an indefinite mixture of various silicates. The dried substance resembles glass in appearance; it is slowly soluble in hot water, the rate and extent of solution increasing with the proportion of alkali to silica. On adding alcohol to the concentrated solution, a salt of the composition $2Na_2O.9SiO_2.H_2O$ is obtained. Solutions of alkaline silicates are decomposed by all acids; on exposure to air the liquid becomes covered with a pellicle of silica, due to the action of carbonic acid. A very dilute solution, however, is not rendered turbid by the addition of hyrochloric acid, since the silica remains dissolved (see p. 262, Vol. I.).

The use of sodium silicate in preserving and hardening stone depends partly upon the gradual liberation of insoluble silica by the action of atmospheric carbonic acid, and partly upon the formation of insoluble double silicates of lime and magnesia. In painting, the solution of water-glass is mixed with the colours previously ground with water, and the mixture is applied in the ordinary manner; the addition of a solution of alumina in potash (so-called aluminate of potash) to the water-glass prevents, in a great measure, the efflorescence, due to sodium carbonate, which is apt to form on the painted surface. Water-glass has been applied to diminish the combustibility of wood, as a detergent in wool-cleansing, and as a dung-substitute in dyeing calico.

Sodium compounds may be detected by the yellow colour which they impart to the non-luminous flame of the Bunsen lamp. In the spectroscope this light affords a yellow line coincident with the Fraunhofer line D. Meta-antimoniate of potassium, $K_2Sb_2O_6.7H_2O$, gives, with moderately concentrated solutions of sodium compounds, a white flocculent precipitate, which becomes crystalline on standing.

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44. **Potassium**—Symbol K; atomic weight, 39·1.—Potash was distinguished from soda by Duhamel in 1736, and, more completely, by Marggraf in 1758. Its compounds are very widely distributed in nature. In combination with silica, it is found in felspar and mica; as the nitrate, it occurs in the soils of many tropical countries, and the sulphate and chloride are found in certain saline deposits. Sea-water also contains potassium salts. Potash, combined with organic acids, occurs as an essential constituent of the inorganic portions of many plants and trees, and of many organs and juices of animal organisms.

A large portion of the potash which is found in commerce is obtained from the ashes of forest trees. In North America, Russia, Norway and Sweden, and in other countries where large forests occur, the trees are burnt in pits or in piles, and the ash which remains is lixiviated with water; the solution, evaporated to dryness in flat iron or copper pans, yields crude "pot-ashes," consisting chiefly of potassium carbonate, sulphate, and chloride, together with empyreumatic substances and moisture. By calcining the crude potashes, the moisture and empyreumatic matter are expelled, and the ash becomes white, and the product is now known as "pearl-ash." In order still further to purify it, the calcined product is dissolved in water, the solution is concentrated, and the more insoluble salts allowed to crystallise out; the still liquid portion evaporated to dryness, yields "refined pearl-ash."

Considerable quantities of potash are obtained by the incineration of marine plants. The method of treating the "kelp," or ash of sea-weeds, for the potassium salts which it contains has already been described in Vol. I., p. 285.

Potassium chloride is procured from a large deposit of a double chloride of magnesium and potassium, termed *carnallite*, found in the salt beds of Stassfurth in Prussia. This double salt, which has the composition $KCl.MgCl_2.6H_2O$, is decomposed by treatment with water: on concentrating the solution, a large proportion of the potassium chloride separates out, the more soluble magnesium chloride remaining in solution. The solution containing the remainder of the potassium chloride, on a further evaporation, again yields crystals of carnallite, which are again treated with water to effect a further separation of the two chlorides.

Similar deposits of potassium salts have been discovered in East Galicia, chiefly as *sylvine* (potassium chloride) and *kainite* (a mixture of magnesium sulphate and chloride with potassium sulphate).

Potash salts are also obtained from residues procured in the manufacture of beetroot sugar: the uncrystallisable saccharine liquors or molasses are diluted and allowed to ferment, and the alcohol thus obtained is separated by distillation. The residue is neutralised with chalk and allowed to settle, the clear solution is evaporated to dryness, and the saline mass calcined.

The sweat of animals feeding on grass contains potash in union with a nitrogenous acid. The potassium *sudorate*, as this compound is termed, is found in raw wool to the extent of about 14 per cent., and may be extracted by simply washing with water. The solution is evaporated to dryness, and the residue calcined; on treatment with water, the potassium salts are obtained in solution nearly pure.

Potassium was first obtained by Sir H. Davy in 1807, by the electrolytic decomposition of the hydrate. A piece of caustic potash placed on a plate of platinum connected with the positive pole of a powerful galvanic battery, was allowed to deliquesce, so as to increase its conductivity; it was then touched with a platinum wire connected with the negative pole of the battery, when it rapidly liquefied and was decomposed; the globules of metallic potassium formed were quickly removed and immersed in petroleum to prevent oxidation.

Shortly after its discovery by Davy, Gay-Lussac and Thenard showed that the metal might be obtained more readily by passing fused potassium hydrate over iron borings heated to whiteness; the iron became oxidised at the expense of the hydrate, and hydrogen and potassium were liberated. By passing the vapours through a cooled receiver *d* (fig. 110) containing rock oil, the potassium was condensed.

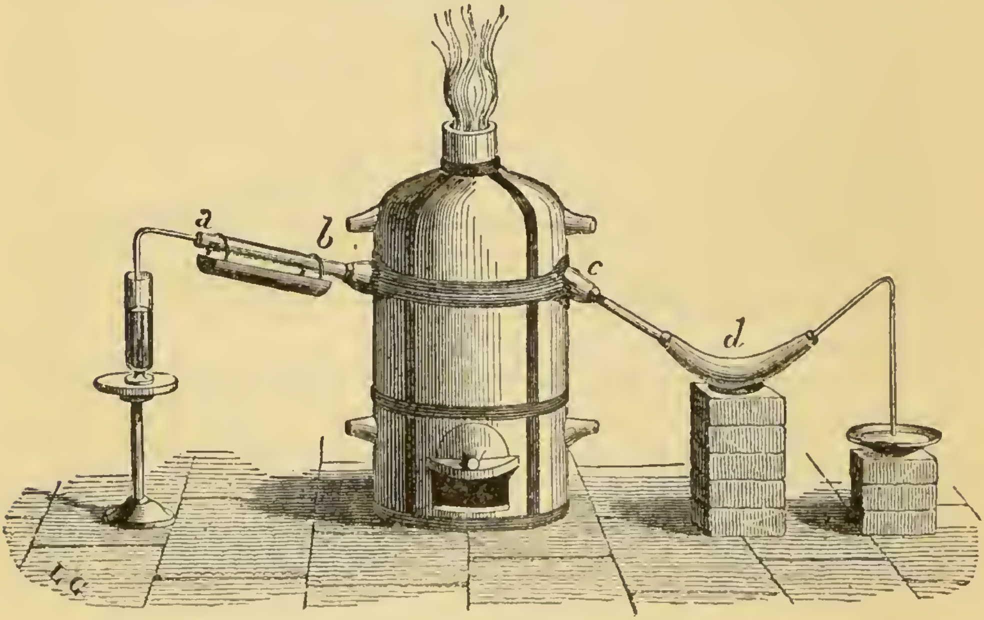

Fig. 110.

Potassium is now obtained by decomposing the carbonate by means of charcoal at a full red heat. Fig. 111 represents the apparatus usually employed. The cylindrical iron vessel is filled with a mixture of potassium carbonate and charcoal, obtained by igniting crude tartar. It is heated to a low redness, and when the vapour of potassium begins to appear at the mouth of the tube, the receiver (seen in section in fig. 112) is adapted to it. The receiver is made of this flattened form in order to facilitate the condensation and cooling of the metal, and thus to obviate the formation of a dangerously explosive combination of potassium and carbon monoxide. The reaction may be thus represented:

$$K_2CO_3+C_2=K_2+3\,CO.$$

although rarely as much as half the theoretical yield of potassium is obtained.

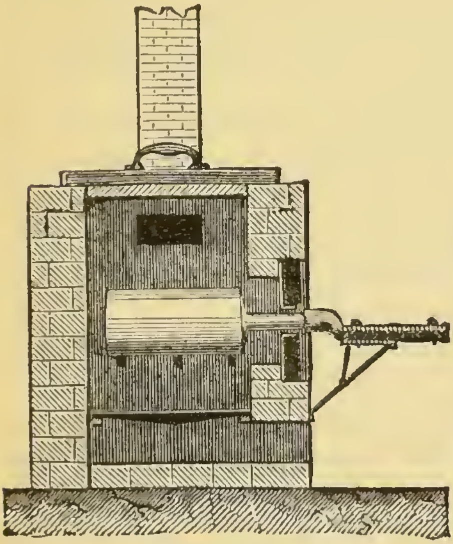
Fig. 111.

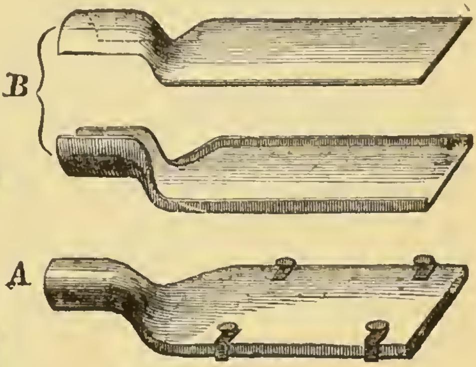

Fig. 112.

Potassium is a white metal with a slight tinge of pink (comp. p. 80). It instantly tarnishes on exposure to air, and its characteristic lustre can only be preserved by keeping it in a sealed tube free from oxygen or beneath the surface of naphtha. It may be obtained crystallised, by melting it in an atmosphere of coal-gas, leaving it to solidify partially, and pouring away the still liquid portion. In the solidified portion are seen numerous quadratic octahedrons. Its specific gravity is 0·865; hence, when thrown upon water, it swims upon its surface. The water, however, is instantly decomposed, hydrogen being rapidly disengaged: the heat evolved is sufficient to inflame the gas, which burns with a violet flame from the volatilization of a portion of the potassium. At low temperatures, potassium is brittle and crystalline, but when gently heated it becomes soft, so that two freshly-cut pieces may be welded together: it melts at 62°, and volatilises at a red heat, yielding a green vapour. It unites with sulphur, selenium, phosphorus, and the halogens, with incandescence. Ammonia gas rapidly acts upon potassium, forming an olive green crystalline powder, termed *monopotassamide*, of the composition KH_2N. When heated out of contact with air, it evolves ammonia, and is converted into *tripotassamide*, a dark green substance, having the formula K_3N. Potassium combines readily with many metals, but the alloys are of no practical importance. The combination with sodium is liquid at ordinary temperatures, and bears a striking resemblance to mercury.

45. Potassium Hydride.—Melted potassium, at a temperature of 400°, absorbs hydrogen, and is converted into a lustrous, brittle, crystalline body, resembling silver amalgam. Its composition is K_2H. It may be melted in hydrogen or in a vacuum without alteration, but on exposure to air it ignites. At a high temperature the hydride is decomposed, and by removing the gas as it is liberated, the whole of the hydrogen may be rapidly extracted from the metal.

46. Potassium Oxides.—Three oxides of potassium are stated to exist, the **monoxide** K_2O, the **dioxide** K_2O_2, and the **tetroxide** K_2O_4. The monoxide is a white, highly deliquescent, fusible powder, obtained by exposing the metal to dry oxygen, or by heating the hydrate with potassium.

$$2KHO + K_2 = 2K_2O + H_2.$$

The tetroxide is a yellow powder, formed by heating the metal, first in dry air, and then in oxygen gas. When strongly heated in nitrogen in contact with silver, it parts with oxygen, and is converted into the monoxide. By treatment with water it is decomposed with loss of oxygen, and formation of the dioxide.

47. Potassium Hydrate or **Caustic Potash,** KHO, is formed by the action of the metal upon water—

$$K + H_2O = KHO + H.$$

It is usually prepared by boiling a moderately dilute solution of potassium carbonate with slaked lime. One part of the carbonate dissolved in twelve parts of water is heated to boiling in an iron pot, and two parts of lime previously slaked in nine parts of water is added by degrees, the liquid being boiled for a few minutes after each addition of the lime, in order to insure its conversion into calcium carbonate. When the whole of the lime has been added, the solution is boiled for a quarter of an hour, allowed to clarify by standing, the clear liquid drawn off and boiled down in a silver basin until the hydrate begins to evaporate. The oily liquid is then run into cylindrical moulds in which it solidifies, forming the sticks sold in the shops as *potassa fusa* (fig. 113).

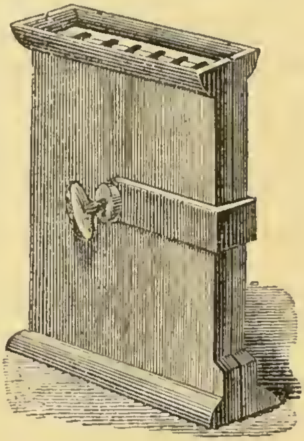
Fig. 113.

Caustic potash as thus prepared commonly contains more or less alumina, silica, oxide of iron, and calcium and potassium carbonates, the last-named compounds being due to careless decantation or imperfect decomposition. If in the preparation the solution is allowed to become concentrated whilst still in contact with calcium carbonate, potassium carbonate may be regenerated, since a strong solution of potash boiled with chalk forms calcium monoxide and potassium carbonate. The potash may be purified by treatment with alcohol, in which it readily dissolves, the greater number of the impurities remaining undissolved.

Pure potassium hydrate may also be obtained by decomposing a solution of the sulphate with an equivalent amount of baryta, or by heating the nitrate to redness with metallic copper, or better, iron, in a covered iron crucible; on heating the deflagrated mass with water, potassium hydrate is formed, and may be dissolved out from the cupric or ferric oxides.

Caustic potash readily absorbs moisture and carbon dioxide. It is soluble in about half its weight of water and alcohol, and in the act of solution evolves great heat. On cooling, a concentrated aqueous solution, acute rhombohedrons of the composition $KHO.2H_2O$, is deposited. The solution is intensely caustic, and occasions a soapy feeling when rubbed between the fingers, from its action on the cuticle. It rapidly acts on animal and vegetable matter, and therefore cannot be filtered through paper. Large quantities of potash are used in the arts, by glassmakers, soap-boilers, and others; it is of great use in the laboratory as a precipitant, and as an absorbent for certain gases.

48. Potassium Chloride, KCl, is found in sea-water, and in many mineral springs. It exists in *kelp;* this material, indeed, constitutes one of the chief sources of supply of potash compounds (see Vol. I., p. 286). Potassium chloride crystallises in cubes, which are anhydrous; large crystals are occasionally found native, constituting the mineral known as *sylvine.* It dissolves in about three parts of water at ordinary temperatures, with the production of great cold. It fuses at 738°. It absorbs sulphur trioxide, forming a hard shining mass of the composition $\left.\begin{matrix}SO_2\\K\end{matrix}\right\}\begin{matrix}O\\Cl\end{matrix}$, analogous to sulphuryl hydroxyl chloride, $\left.\begin{matrix}SO_2\\H\end{matrix}\right\}\begin{matrix}O\\Cl\end{matrix}$ (see Vol. I., p. 348). A similar product is formed with chromic trioxide, $\left.\begin{matrix}CrO_2\\K\end{matrix}\right\}\begin{matrix}O\\Cl\end{matrix}$.

49. Potassium Bromide, KBr, also occurs in many mineral waters. It is readily formed by dissolving the carbonate or the hydroxide in hydrobromic acid, or by adding bromine to a solution of potash, treating the liquid with sulphuretted hydrogen to decompose the bromate produced, filtering from the precipitated sulphur, and evaporating the solution. The salt crystallises in cubes, and is readily soluble in water at ordinary temperatures. It fuses at 703°.

50. Potassium Iodide, KI, is obtained by dissolving the hydroxide or carbonate in hydriodic acid, or by adding iodine to a solution of caustic potash until the liquid acquires a brown tint, when potassium iodide and iodate are simultaneously formed—

$$3I_2 + 6HKO = 5KI + KIO_3 + 3H_2O.$$

On evaporating the solution to dryness, and gently igniting the residue, the iodate is converted into iodide. It fuses at 639°, and dissolves in less than its own weight of water, and in about five parts of alcohol at ordinary temperatures; its solution dissolves iodine freely, forming a dark brown liquid. Potassium iodide frequently contains iodate; the latter salt may be readily detected by adding a little starch paste to its solution, and then a few drops of dilute hydrochloric acid free from chlorine; if iodic acid be present, the liquid acquires a deep blue colour.*

51. **Potassium Sulphides.**—Potassium combines with sulphur in several proportions. The **monosulphide**, K_2S, is said to be formed by heating normal potassium sulphate in hydrogen, or with finely-divided charcoal. It is described as an orange-coloured, exceedingly hygroscopic powder, possessing a strong alkaline reaction. It is doubtful, however, if it has been obtained pure.

The **disulphide**, K_2S_2, is prepared by exposing a solution of the sulphydrate to air or to oxygen; the colourless solution quickly becomes yellow from the absorption of oxygen and formation of the higher sulphide—

$$2HKS + O = K_2S_2 + H_2O.$$

It may be obtained by evaporation *in vacuô*, as a reddish yellow powder.

52. **Tri-, Tetra-, and Penta-sulphides of Potassium** are known. They enter into the composition of the *liver of sulphur* of pharmacy, a substance prepared by heating a mixture of potassium carbonate and sulphur.

53. **Potassium Sulphydrate**, KHS, may be formed by the action of the metal upon sulphuretted hydrogen,

$$K + H_2S = KHS + H,$$

a reaction precisely analogous to that of the metal upon water. It is also obtained by saturating an aqueous solution of potash with sulphuretted hydrogen.

54. **Dipotassium Sulphate**, K_2SO_4, is found native, in thin prismatic crystals, as *glaserite*. It occurs in sea-weed, and is now largely obtained from kelp. It crystallises in forms derived from the rhombic system. Fig. 114 represents one of its principal forms. The **plate sulphate** of commerce has the composition $K_3Na(SO_4)_2$, it forms plates or

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* Hydrochloric acid frequently contains small traces of free chlorine, which would bring about the blue colouration of the starch from the liberation of the iodine, even if an iodate were absent. The error from this cause may be avoided by placing a crystal of tartaric acid in the solution of the salt under examination; the presence of iodic acid is revealed by the formation of a yellow zone round the crystal.

prisms belonging to the hexagonal system. A bright flash of light is frequently observed to attend the separation of each crystal from the solution.

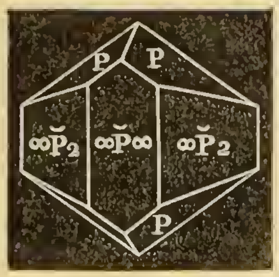

Fig. 114.

Normal potassium sulphate is sparingly soluble in water (one part of salt in about nine of water); it is insoluble in absolute alcohol. By dissolving the salt in strong nitric acid, four-sided prisms of the combination $K_2SO_4.HNO_3$ are obtained. With phosphoric acid a compound of the formula $K_2SO_4.H_3PO_4$ is obtained. When heated with sulphuric anhydride, the normal sulphate gives the **anhydro-sulphate** $K_2S_2O_7$; with Nordhausen acid, the **hydro-potassium anhydro-sulphate** KHS_2O_7 is formed; it crystallises in prisms, and melts at 168°.

The **acid sulphate**, $HKSO_4$, is also found native as *misenite*, and is obtained in the laboratory as a bye-product in the preparation of nitric acid. It dissolves much more readily in water than the normal salt, and crystallises in rhombic octahedrons, resembling those of sulphur. The salt is, however, dimorphous, and may be obtained in monoclinic prisms similar to those of felspar.

55. **Potassium Nitrate, Nitre,** or **Saltpetre,** KNO_3, occurs in considerable quantity in the soils of many countries, as in certain parts of India, Persia, Arabia, and Spain; indeed, it is probably present in small quantity in nearly all soils. It is frequently met with in small quantity in calcareous formations; the spring-waters rising from such formations often contain notable quantities of nitrates. Nitrates are also frequently observed, as an efflorescence, in the caves which abound in limestone districts.

In Bengal, where large quantities of nitre are found, the surface-soil is carefully removed and treated with water, the solution is allowed to clarify by standing, and is boiled down. The crude saltpetre thus obtained contains considerable quantities of alkaline chlorides and organic matter, which are removed by treatment with a quantity of hot water sufficient to dissolve the nitrate. Since potassium nitrate is much more soluble in hot water than sodium chloride, the greater portion of the latter salt is left undissolved. The solution separated from the residual salt is diluted and boiled with glue, the organic matter is thus coagulated, and rising to the surface, is skimmed off. The liquid is concentrated, and, when the nitre commences to separate out, it is rapidly agitated in order to prevent the formation of large crystals and their consequent contamination with the chlorides, etc., still remaining in the mother-liquor. The *saltpetre-flour*, as the crystalline powder thus obtained is termed, is washed with a saturated solution of pure nitre in order to remove the adhering mother-liquor, and is then dried.

Considerable quantities of potassium nitrate are obtained from Chili saltpetre or sodium nitrate. The latter salt is dissolved in water, and added to a hot concentrated solution of pearl-ash. Sodium carbonate is thrown down, and the nitre formed remains in solution; on concentration it is obtained in crystals. Occasionally the pearl-ash is previously treated with lime, and the caustic potash thus formed is added to the solution of the nitrate: on boiling and concentrating, the potassium nitrate separates out, caustic soda remaining in solution. Nitre may also be formed by boiling solutions of potassium chloride and Chili saltpetre, the sodium chloride thus produced is precipitated when the liquid is sufficiently concentrated, the nitre being obtained from the mother-liquor by further evaporation.

On the Continent, saltpetre is formed artificially by the decomposition of nitrogenous organic matter. A large heap, consisting of ashes mixed with animal matter and lime, is watered at intervals with urine or the drainage from stables. After a sufficiently lengthened exposure to air, the earth is lixiviated, and the nitrates, formed by the oxidation of the nitrogenous matter, are dissolved out: the solution is mixed with potash carbonate added in the form of wood ashes, in order to decompose the calcium and magnesium nitrates. The liquid is clarified by standing; on evaporation it yields crude nitre, which is refined by the method above described.

Pure potassium nitrate is a white salt, possessing a bitter taste. It is soluble in about $3\frac{1}{2}$ parts of water at 18°, and in less than $\frac{1}{2}$ part at 100°. It is perfectly insoluble in absolute alcohol. It generally crystallises in rhombic prisms (fig. 115), but it may also be obtained in forms resembling those of calc-spar. Potassium nitrate melts at 358°, and solidifies to a white fibrous mass, known in pharmacy as *sal-prunellæ.* It gives off oxygen at a red heat, and is converted into potassium nitrite; at higher temperatures it parts with nitrogen, and leaves a mixture of mono- and dioxide of potassium. Nitre contains nearly half its weight of oxygen, which it readily loses when heated with oxidisable substances. Thus, when mixed with certain finely-divided sulphides the mass deflagrates on being heated, and potassium sulphate is formed. *Touch-paper*, which is largely used in the manufacture of fireworks, is simply paper dipped in a solution of nitre and dried.

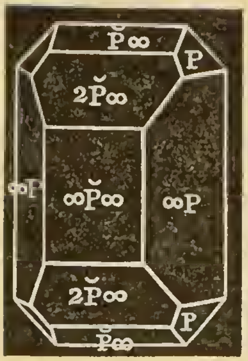

Fig. 115.

Gunpowder.—Potassium nitrate enters largely into the composition of gunpowder, which is a mechanical mixture of sulphur, charcoal, and nitre. Its projectile and disruptive force depend upon the facility with which it burns, the high temperature of its combustion, and the effect of the heat on the large volume of gas which is generated. Gunpowder is made by mixing refined nitre, ground sulphur, and powdered charcoal, made from willow, dog-wood, or alder, in the proper proportions in a revolving drum, whereby they become intimately blended. The mixture is made into a stiff paste with water, and is ground under stones; the mass thus obtained is subjected to intense pressure, and the hard sonorous block, technically known as *press-cake*, is granulated whilst still damp by the action of toothed rollers, and is passed through sieves, whereby it is sorted into grains of various sizes. The sifted powder is then dried in steam chests, and the grains are polished by being agitated one against the other in a revolving barrel. Large-grained powder, such as is employed in mining operations, is frequently glazed by the addition of a little powdered graphite to the barrel. The value of the powder as an explosive agent bears an intimate relation to its gravimetric density; the heavier it is, the greater is its projectile force. The relative proportions of the various constituents vary with the use to which the powder is put: blasting powder, for example, always contains more sulphur than ordnance powder. The following Table exhibits the composition of certain ordnance powders:—

		English Rifle.		Russian.		Chinese.
Saltpetre,		75·04		74·18		61·5
Sulphur,		9·93		9·89		15·4
Charcoal,	Carbon,	10·67	14·09	10·75	14·83	23·1
	Hydrogen,	0·52		0·43		
	Oxygen,	2·66		3·31		
	Ash,	0·24		0·34		
Moisture,		0·80		1·10		
		99·86		100·00		100·0

When gunpowder is fired it is resolved into gases and into matter which ultimately becomes solid; but it is impossible to express the exact nature of the decomposition in the form of an equation, since it varies with the conditions under which the powder is fired. When one gram of powder of the ordinary gravimetric density (about 1) is fired in a closed space, it is resolved into about 0·43 grm. of permanent gases, which at the moment of explosion occupy about 0·4 cubic centimetres, and 0·57 grm. of matter which ultimately solidifies, and which as a liquid occupies about 0·6 cc. The volume of the permanent gas formed, measured at 0°, and under a pressure of 760 mm. is about 280 times that of the powder.

GASES.

Carbon dioxide,	52·40
Carbon monoxide,	8·86
Sulphuretted hydrogen,	1·60
Nitrogen,	34·51
Methane,	0·12
Hydrogen,	2·51
	100·00

SOLIDS.

Potassium Carbonate,	58·94
,, Sulphate,	21·89
,, Thiosulphate,	8·15
,, Monosulphide,	4·22
,, Sulphocyanate,	0·04
,, Nitrate,	0·06
Ammonium Carbonate,	0·06
Sulphur,	6·65
	100·01

The percentage composition by volume of the gas, and by weight of the solid residue, are stated above. The powder is "English rifle," the composition of which is given above: the charge occupies about seven-tenths of the space in which it is fired.

The tension of the products of combustion, when the powder entirely fills the space in which it is fired, has been variously estimated, but the researches of Noble and Abel show that it may be taken at about 6400 atmospheres, or about 42 tons on the square inch. The temperature of the explosion is estimated at about 2200°C. (Noble and Abel, *Phil. Trans.* 1875.)

56. **Dipotassium Carbonate,** K_2CO_3, is obtained by lixiviating the ashes of plants. The potash exists in the plants in union with vegetable acids, which are destroyed on incineration, the salts being converted into carbonate. The quantity of potash varies considerably in different parts of the plant; as a rule, herbaceous and succulent plants yield more than shrubs or trees: the amount of potash varies also in different parts of the same plant; it is present in largest quantity in the leaves, and in least quantity in the wood.

Pure potassium carbonate may be obtained by deflagrating a mixture of pure potassium tartrate and nitrate; on treating the mass with water, potassium carbonate dissolves out. A better method consists in recrystallising the acid carbonate, $KHCO_3$, and igniting it in a platinum crucible.

Potassium carbonate dissolves in about its own weight of water at common temperatures, and gives a strongly alkaline solution, which, on concentration, deposits the salt in rhombic octahedrons of the composition $K_2CO_3.2H_2O$. The anhydrous salt is highly deliquescent, it melts at 838°, and may be volatilised without decomposition.

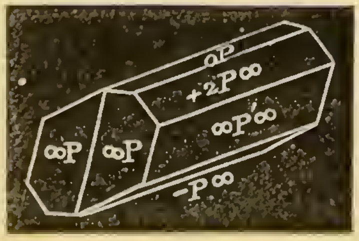

Fig. 116.

57. **Monopotassium Carbonate,** or **acid potassium carbonate,** $KHCO_3$, is formed by treating the dipotassium salt, either in the solid state or in solution, with carbon dioxide. It forms large, well-developed prisms belonging to the monoclinic system (fig. 116). It dissolves in about four

times its weight of water at ordinary temperatures; on being boiled the solution loses carbon dioxide, and the salt is gradually changed into the normal carbonate. The same salt is also formed by heating the crystallised acid-salt to 100°.

58. Potassium Silicates.—These compounds resemble the corresponding salts of sodium, and they are prepared by similar methods. *Apophyllite* is a double silicate of potassium and calcium, associated with calcium or potassium fluoride. Double silicates of potassium, aluminium, and iron, enter into the composition of many well-known minerals, as *leucite, orthoclase, prehnite, harmotome,* etc.

Potassium compounds are characterised by the violet colour which they impart to the non-luminous gas flame, affording in the spectroscope two lines in the red, one coincident with the Fraunhofer line A, and a line in the violet near H. Solutions of potassium compounds, when moderately concentrated, give a white precipitate with tartaric acid of cream of tartar, $KH_5C_4O_6$; and a yellow crystalline precipitate with platinum tetrachloride, consisting of K_2PtCl_6. The addition of alcohol promotes the separation of these precipitates.

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59. Rubidium—Symbol Rb; atomic weight 85·4.—This element was discovered by Bunsen in 1860, in the mineral water of Dürkheim, in which it exists to the extent of one part in five millions. Since that time its presence has been demonstrated in many other mineral waters, notably in those of Nauheim and Bourbonne-les-Bains. It occurs in many lepidolites and in other lithia minerals; in the ashes of many plants; in coffee, tea, cocoa, etc. Rubidium almost invariably accompanies potassium and cæsium, and, occasionally, thallium. The chlorides of these bodies, obtained from the residues in the extraction of lithia from lepidolite, are converted into platino-chlorides, and treated repeatedly with small quantities of hot water, whereby the more soluble potassium compound is dissolved out; the residue is dried and heated in hydrogen, and the chlorides of rubidium and cæsium are separated from the reduced platinum by boiling water. The chlorides are treated with sulphuric acid, and the resulting sulphates converted into the alums, the solubilities of which vary greatly at ordinary temperatures. Thus at 17°, 100 parts of water dissolve of

Potassium-alum.	Rubidium-alum.	Cæsium-alum.
13·5 parts.	2·27 parts.	0·619 part.

Hence the potash alum is nearly 6 times more soluble than the rubidium alum, and 22 times more soluble than the cæsium compound (Redtenbacher). By means of these differences in solubility, it is comparatively easy to separate the cæsium and rubidium from the last traces of potassium, and from each other.

Another method, given by Bunsen, is to convert the sulphates into carbonates, by treatment with baryta water and carbonic acid, and the carbonates into tartrates. The latter salts are placed in a funnel in an atmosphere saturated with moisture; the cæsium compound rapidly deliquesces, and drops as a concentrated solution from the end of the funnel, leaving a residue of acid tartrate of rubidium.

Bunsen, by distilling the charred acid-tartrate, obtained rubidium as a silver-white metal of specific gravity 1·52, melting at 38·5, and as soft as wax even at 10°; it readily volatilised, and afforded a greenish-blue vapour. It is more rapidly oxidised than potassium in contact with air, taking fire on exposure; it decomposes water with great violence, evolving spontaneously inflammable hydrogen, and forming **rubidium hydrate**, which on evaporation is left as a white porous fusible mass, volatile at a high temperature, highly deliquescent, and soluble in alcohol and water, with rise of temperature.

60. Rubidium Chloride, RbCl, forms cubic crystals of a vitreous lustre, anhydrous, and non-deliquescent, properties which belong also to the bromide and iodide.

The **chlorate**, **perchlorate**, and the **neutral** and **acid chromates**, are isomorphous with the corresponding potassium salts which they greatly resemble. The **nitrate** crystallises in hexagonal combinations, and is soluble in about 2·3 parts of water at ordinary temperatures. **Rubidium sulphate**, Rb_2SO_4, is anhydrous and isomorphous with potassium sulphate; it forms an *alum*, $AlRb(SO_4)_2.12H_2O$; and produces hexahydrated double salts with the sulphates of magnesium, cobalt, nickel, analogous to the corresponding potassium salts.

Rubidium may be detected by the occurrence of two lines in the red, less refrangible than A, whence its name, from *rubidus;* two in the orange between C and D; two in the yellow; two in the green, on either side of E; and two in the violet, less refrangible than Kβ. Its platinochloride is less soluble than the corresponding potassium salt, but more soluble than the cæsium compound: 100 parts of water at 17° dissolve

K_2PtCl_6.	Rb_2PtCl_6.	Cs_2PtCl_6.
1·12 parts.	0·141 part.	0·079 part.

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61. **Cæsium**—Symbol Cs; atomic weight 133.—Discovered by Bunsen in 1860, in the Dürkheim mineral water, and since found in many other springs, notably in that of Wheal Clifford in Cornwall. It is present in many lepidolites, and in the ashes of several plants; it constitutes about 32 per cent. of the rare mineral *pollux*, found in Elba. The metal has not yet been prepared, but an amalgam of it may be obtained in the manner indicated on p. 48. Cæsium is the most electropositive element known. The **hydrate**, CsHO, is a deliquescent caustic body, easily soluble in alcohol. The **chloride** crystallises in cubes which volatilise on heating. The **sulphate** is anhydrous, more soluble than potassium sulphate, and readily forms an alum. The **nitrate** is anhydrous and isomorphous with the rubidium salt, and not with potassium nitrate. The **carbonate** is deliquescent and soluble in alcohol and water; the acid-tartrate is also soluble in water. By the characters of the two last-named salts, cæsium may be distinguished from rubidium and potassium; its spectral indications are two bright lines in the blue, whence its name from *cæsius*, sky-blue; three in the green, less refrangible than E; two in the yellow, and two in the orange; the highly characteristic blue lines of the flame spectrum are absent in the spark spectrum.

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62. **Ammonium.**—This name is applied to a hypothetical basic radicle NH_4, which is assumed to combine with acid radicles, *e.g.*, SO_4, NO_3, Cl. etc., to form salts, many of

which are both chemically and physically analogous to the corresponding salts of potassium. This radicle has not been isolated; it is doubtful, indeed, if it can exist in the free state. When a solution of ammonium chloride is poured over sodium amalgam, a soft slimy mass is formed, which swells up to many times the original bulk of the sodium amalgam. This curious substance has been termed an **ammonium-amalgam**, on the assumption that it was a combination of the radicle NH_4 with mercury. In reality, however, it is nothing but a mercurial froth, inflated with a mixture of ammonia and hydrogen. The metalline mass on being subjected to pressure changes its volume like a gas; by strong compression it assumes the ordinary appearance of mercury; but on releasing the pressure the imprisoned gases expand to their original volume, and the mass again acquires a dull frothy aspect. The so-called ammonium amalgam has no action on solutions of silver or copper salts, whereas the amalgams of sodium and potassium displace the silver or copper. When dry ammonia is brought into contact with sulphur trioxide, a white crystalline powder of the composition $N_2H_6SO_3$ is formed. This body is termed **ammonium sulphamate**; its constitution may be expressed by the formula $SO_2\left\{\begin{matrix}NH_2\\NH_4\end{matrix}\right.$; it is the ammonium salt of an acid derived from sulphuric acid, $SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, by the replacement of hydroxyl by the radicle amidogen, NH_2. Ammonium sulphamate is readily soluble in water, and may be obtained in crystals by evaporation *in vacuo*. Baryta-water liberates ammonia and forms **barium sulphamate**, $Ba(SO_3NH_2)_2$; it is a soluble salt which, on the addition of potassium sulphate, yields **potassium sulphamate**, SO_3NH_2K, and barium sulphate.

A similar compound, termed **carbamic acid**, is formed by the union of carbon dioxide and ammonia gas; it has the composition $\overset{II}{CO}\left\{\begin{matrix}NH_4\\NH_2\end{matrix}\right.$, and may be regarded as the ammonium salt of an acid derived from carbonic acid, $\overset{II}{CO}\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, by the substitution of amidogen for hydroxyl. By replacing both hydroxyl groups by amidogen, *carbamide* or *urea* is obtained, $CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$. This replacement can be effected by the action of ammonia on phosgene gas, $CO^{II}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$—

$$COCl_2+4NH_3=2NH_4Cl+CON_2H_4.$$

Most bibasic acids appear to be capable of forming a corresponding *amic acid* and an *amide;* tribasic acids form two amic acids and an amide; tetrabasic acids form three amic acids and one amide. On the other hand, monobasic acids yield an amide, but no amic acid.

The action of ammonia upon the acids is very different from its behaviour with the acid radicles. Thus with sulphuric acid it forms the compound $(NH_4)_2SO_4$—

$$2NH_3+H_2SO_4=(NH_4)_2SO_4,$$

with nitric acid it forms NH_4NO_3; with hydrochloric acid, NH_4Cl—

$$\begin{aligned}NH_3+HNO_3&=NH_4NO_3\\NH_3+HCl\ \ &=NH_4Cl.\end{aligned}$$

63. **Ammonium Chloride, or Sal-Ammoniac,** NH_4Cl.—When hydrochloric acid gas and ammonia gas are mixed together in equal volumes, dense white fumes of ammonium chloride are produced, which condense to form aggregations of minute cubical or octahedral crystals. Sal-ammoniac is frequently found as a product of volcanic action. It was formerly almost exclusively obtained from Egypt, where it was prepared by heating the soot obtained by burning camels' dung. It is now manufactured by neutralising the ammonia water of the gas works with hydrochloric acid, evaporating the solution, and subliming the residue. It is thus obtained in tough, fibrous masses. It is soluble in about $2\frac{3}{4}$ parts of water at ordinary temperatures, with considerable reduction of temperature. Its solution gradually becomes acid on boiling from loss of ammonia. It is readily volatilised, and on being strongly heated dissociates into ammonia and hydrochloric acid gases, which recombine on cooling.

64. **Ammonium Sulphides.**—The **normal sulphide,** $(NH_4)_2S$, may be obtained in colourless crystals by mixing, at a low temperature, sulphuretted hydrogen, with twice its volume of ammonia gas. At ordinary temperatures the salt

evolves ammonia, and is converted into **ammonium sulphydrate**, NH_4HS, a solution of which, prepared by passing sulphuretted hydrogen into ammonia water, is much used as a re-agent in the laboratory. The following polysulphides have been obtained—

Disulphide,	$NH_4—S—S—NH_4$
Trisulphide,	$NH_4—S—S—S—NH_4$
Tetrasulphide,	$NH_4—S—S—S—S—NH_4$
Pentasulphide,	$NH_4—S—S—S—S—S—NH_4$
Heptasulphide,	$NH_4—S—S—S—S—S—S—S—NH_4$.

The heptasulphide is the most stable member of the series, and is but slowly acted upon by acids. It forms dark red crystals, which may be heated to 300° without decomposition.

The *fuming liquor of Boyle*, obtained by distilling a mixture of sulphur, sal-ammoniac, and lime, consists of a mixture of the above-named sulphides.

65. **Di-Ammonium Sulphate**, $(NH_4)_2SO_4$, is made by blowing steam through the ammoniacal liquor of the gas works and condensing the vapours in sulphuric acid. It crystallises in forms belonging to the rhombic system, and is isomorphous with potassium sulphate. An **acid-sulphate**, NH_4HSO_4, may be obtained by adding the normal salt to dilute sulphuric acid. The ammonium sulphates are principally used in the manufacture of artificial manures, and of ammonia alum.

66. **Ammonium Nitrite**, NH_4NO_2, is best prepared by mixing solutions, in equivalent quantities, of barium nitrite and ammonium sulphate, and evaporating the clear liquid in a vacuum at the ordinary temperature. It is a white, crystalline, elastic, and tenacious substance, readily moulded between the fingers. It slowly decomposes at common temperatures, and detonates when struck with a hammer, or when heated to 60° or 70°. Its concentrated aqueous solution rapidly decomposes on warming, evolving pure nitrogen:

$$NH_4NO_2 = N_2 + 2H_2O.$$

67. **Ammonium Nitrate**, NH_4NO_3, is readily obtained by adding ammonia solution in slight excess to nitric acid. On concentrating the solution, the salt is obtained in hexagonal prisms. It is slightly deliquescent, and dissolves in less than its own bulk of water, with great depression of temperature.

It fuses at 108°, boils at 180°, and between 230 and 250° is decomposed into nitrogen monoxide and water.

68. **Ammonium Carbonates.**—The **normal carbonate** $(NH_4)_2CO_3.H_2O$, is an unstable salt, readily parting with ammonia and water, and changing to the **acid carbonate** NH_4HCO_3 even in solution; indeed, it appears that the salt cannot be dissolved in water without more or less decomposition into the acid carbonate and free ammonia. The latter salt, known also as *bicarbonate of ammonia*, has been found in guano, and is occasionally met with in brilliant rhombic crystals in the purifiers of the gas manufactories; it may be obtained by saturating a solution of ammonia with carbonic acid. It is dimorphous; its principal forms belonging to the rhombic system. It has an ammoniacal smell, and its solution loses ammonia even at ordinary temperatures.

Tetrammonium Dihydrogen Carbonate, or *sesquicarbonate of ammonia*, $(NH_4)_4H_2(CO_3)_3$, may be obtained by dissolving either of the preceding salts in strong solution of ammonia.

The ammonium carbonate of commerce is a mixture of the acid-carbonate and the carbamate. It is obtained on the large scale by the distillation of nitrogenous organic matter; the crude substance thus formed is purified by sublimation. It may also be formed by heating a mixture of chalk and sal-ammoniac.

Ammonium salts give similar reactions to the potassium compounds with platinum tetrachloride and tartaric acid. They are readily distinguished, however, by their volatility, and by their yielding ammonia, recognised by its pungent smell, on being heated with caustic soda or lime.

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69. **Silver**—Symbol Ag (Argentum); atomic weight 107·93.—This element has been known from very early times. Its alchemistic symbol was that of the moon, ☾. It is found in the free state in Saxony and Hungary, crystallised in forms derived from the regular system. It also occurs as the chloride (*horn-silver*) in Chili and Peru, as sulphide (*silver-glance*) in many parts of Europe and America, and in smaller quantities as the iodide, bromide,

arsenide, and antimonide. An amalgam of silver is found in Chili, in the Palatinate, in Spain, and Sweden. Many varieties of copper ore and galena contain notable quantities of the metal.

Considerable quantities of silver are extracted from lead in this country by so-called "desilverising processes" (see Lead). It is also obtained in the Hartz from argentiferous copper by fusion with lead, which dissolves out the silver. The mixture of metals is cast into round cakes or discs which are gradually heated on a trough-shaped hearth, termed a liquation-hearth; the lead melts and runs away, and carries the silver with it, the two metals being afterwards separated by cupellation (fig. 117). Mercury readily dissolves silver; a fact which is taken advantage of in the extraction of the metal in Central and South America, and in Saxony. In the Mexican process, the crushed and pounded ore, in which the silver exists partly as metal, partly as chloride and sulphide, is first intimately mixed with common salt, and after standing a few days, a small quantity of roasted and powdered copper pyrites (technically known as *magistral*) is added. The mass is next mixed with mercury, the intermixture being effected by the trampling of mules, and is again allowed to stand; after some days a fresh quantity of mercury is added, and thoroughly incorporated. The silver amalgam, separated by washing away the earthy matter with water, is filtered through canvas, and the pasty amalgam is pressed into solid pyramidal masses, which are heated in the arrangement seen in fig. 118. The

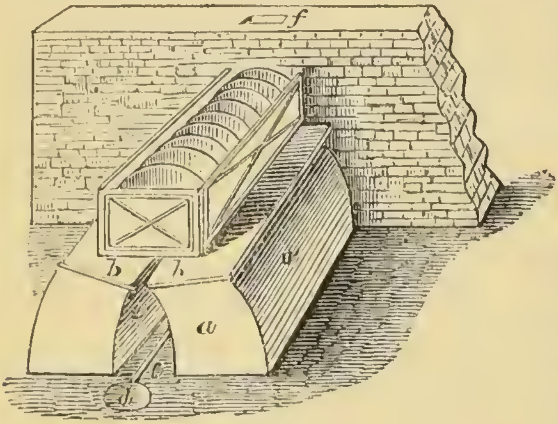

Fig. 117.

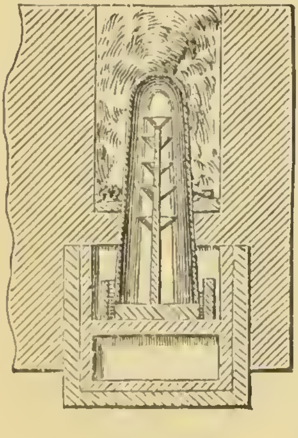

Fig. 118.

amalgam is placed on trays, which are supported on an iron rod standing in a cistern of water. On heating the iron bell, in the manner indicated in the figure, the mercury volatilises, and is condensed in the water, the silver remaining on the trays. The theory of this process of extraction is not perfectly understood, but it is probable that the following reactions take place. The copper sulphate in the roasted pyrites is converted into cupric chloride by the action of the common salt. The cupric chloride reacts upon the silver sulphide, silver chloride and cuprous chloride being formed, and sulphur liberated—

$$2CuCl_2 + Ag_2S = 2AgCl + Cu_2Cl_2 + S.$$

The silver chloride is decomposed by mercury and calomel (Hg_2Cl_2) is formed, and the silver is dissolved in the excess of the mercury. The process occupies from a fortnight to six weeks; it needs careful attention, and the due addition of the magistral, otherwise a great loss of mercury occurs; the amount of mercury needed in any case is very large, since no attempt is made to recover it from the calomel, or from the water used in washing away the earthy matter.

In Spain and Hungary, where mercury is also employed in the extraction of silver, a different method is adopted. The ore—in which the silver exists mainly as sulphide, associated with the sulphides of copper, iron, lead, arsenic, etc.—is ground to powder, mixed with 10 per cent. of common salt, and roasted in a reverberatory furnace at a low red heat. The greater portion of the arsenic and sulphur is expelled, and the silver, copper, and iron are converted into sulphates, and ultimately, by their action on the sodium chloride, into their respective chlorides, sodium sulphate being simultaneously formed. The roasted mass is again ground to powder, and is brought into oaken casks partially filled with water and containing scrap iron (fig. 119). The casks are caused to revolve in order to accelerate the action of the iron on the silver chloride; the silver and copper are thus reduced to the metallic state, and ferrous chloride is formed. A quantity of mercury is now added, and the casks are again set in revolution; the amalgam is then withdrawn and passed through canvas bags; the pasty amalgam is subjected to pressure, and the mercury is distilled off in an iron retort fitted with a condenser (fig. 120) The impure silver left in the retort is melted in plumbago crucibles, and is cast into ingots. It is freed from copper by melting it with lead and cupelling it.

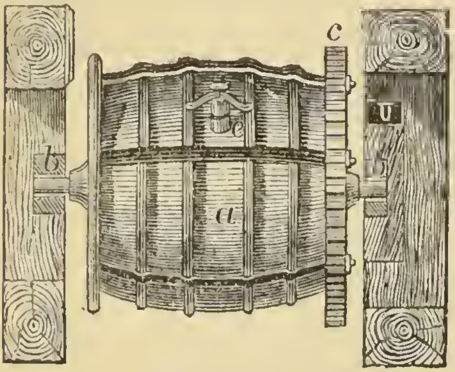

Fig. 119.

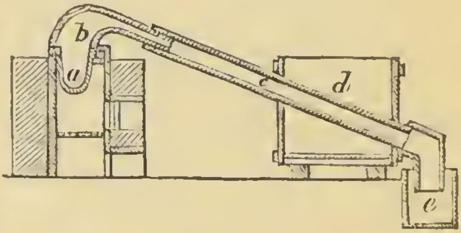

Fig. 120.

Various methods are now in use by which the employment of mercury is obviated. In the method of Augustin, the ore, after having been roasted with common salt, is digested with a strong solution of the same salt, in order to dissolve out the silver chloride, and the metal is precipitated by placing strips of copper in the liquid. Sodium thiosulphate is also used as a solvent for the silver chloride; the silver is precipitated from the solution as sulphide by the addition of sodium sulphide, which is afterwards dried and fused with metallic iron, ferrous sulphide and metallic silver being formed. Ferrous and cupric sulphates are decomposed on heating at a much lower temperature than silver sulphate. It is possible, therefore, by properly regulating the temperature of roasting, to convert the sulphates of iron and copper into oxides, the silver sulphate being undecomposed. The roasted mass is treated with hot water, and the silver is precipitated by metallic copper; this is known as the process of Ziervogel.

Pure silver is a highly lustrous, white metal, exceedingly malleable and ductile; it may be obtained in leaves sufficiently thin to permit of the transmission of bluish-green light. Its conductivity for heat and for electricity is superior to that of any other metal. Its specific gravity is about 10·5, and is increased by hammering. It melts at about 1000°, and may be distilled; its vapour is bluish-purple. When melted it absorbs oxygen from the air, which is expelled again as the metal solidifies. Silver is unacted upon by the air, but in the atmosphere of towns it gradually becomes coated with a film of silver sulphide. It is rapidly dissolved by nitric acid, nitrogen dioxide being evolved; hydrochloric acid has but little action upon it even at the boiling heat; when heated with concentrated sulphuric acid, it yields sulphur dioxide and silver sulphate.

Silver alloys readily with other metals. Indeed, the metal is rarely employed in the arts in a pure state, as it is too soft to resist wear. The silver employed for coinage contains 7·5 per cent. of copper; French silver coin contains 10 per cent. of copper. The addition of the copper increases the hardness of the metal, but has little effect on its colour. Silver readily combines with nickel, and the resulting alloy is highly magnetic; such an alloy is employed for coinage in Switzerland. The alloys with aluminium, gold, and zinc are occasionally used in the arts. The effect on standard silver termed *frosting* is obtained by heating the metal in a current of air whereby a portion of the copper becomes oxidised; on immersion in solution of ammonia, or in dilute sulphuric acid, the oxide is dissolved, leaving the surface dull and lustreless.

The proportion of silver contained in an alloy may be ascertained either by cupellation or by dissolving the alloy in nitric acid, and precipitating the silver as chloride, by the addition of hydrochloric acid or a solution of a chloride. In the former method, a weighed portion of the alloy is melted with lead in a little crucible made of bone earth, termed a *cupel.* The lead and copper are gradually oxidised, and are absorbed by the cupel, and the silver is left in the form of a small button. The operation requires great care and judgment, since many circumstances, such as the temperature to which the cupels are heated, the rapidity of the current of air, the quantity of lead added, etc., exercise an influence upon the result. Greater accuracy may be obtained by the humid method of assay devised by Gay-Lussac. A weighed portion of the alloy is dissolved in nitric acid, and the solution is mixed with a solution of sodium chloride of known strength until no further precipitation of silver chloride ensues. From the volume of the sodium chloride solution required the quantity of the silver is readily calculated.

Silver unites with oxygen in three proportions to form argentous oxide, Ag_4O; argentic monoxide, Ag_2O; and argentic dioxide, Ag_2O_2.

70. **Argentous Oxide** is a black, unstable powder, obtained by heating silver oxalate or citrate in a current of hydrogen.

71. **Argentic Monoxide** is formed by decomposing silver carbonate at a moderate temperature, or by mixing solutions of potash and silver nitrate. It is a dark-brown powder, slightly soluble in water; its solution has an alkaline reaction and absorbs carbonic acid from the air. When heated to 100°, or exposed to strong sunshine, it evolves oxygen; the expulsion of the oxygen is complete at a low red heat. It readily gives up its oxygen when triturated with finely-divided sulphur or phosphorus or sulphide of arsenic; the heat developed by the rapidity of the oxidation is so great that the mass inflames.

72. **Argentic Dioxide** is formed by the electrolysis of a concentrated solution of silver nitrate, or by the action of ozone on finely-divided silver. It is soluble in nitric acid, forming a dark-brown solution; on dilution with water the dioxide is reprecipitated. It is readily decomposed on heating, occasionally with explosion. Hydrochloric acid converts it into silver chloride with elimination of chlorine—

$$Ag_2O_2 + 4HCl = 2AgCl + 2H_2O + Cl_2.$$

Heated with sulphuric acid it forms silver sulphate and oxygen gas. In contact with hydrogen dioxide it forms metallic silver, water, and oxygen—

$$Ag_2O_2 + 2H_2O_2 = Ag_2 + 2H_2O + 2O_2.$$

No silver hydroxide corresponding to caustic potash is known.

73. **Silver Chlorides.**—Two combinations of silver and chlorine are known, but only one, **argentic chloride**, $AgCl$, is of importance. The nature of the other is not exactly determined; it is supposed to have the composition Ag_2Cl or Ag_4Cl_2, and hence is termed **argentous chloride**. It is a brown powder, formed by the action of hydrochloric acid on argentous oxide, or by mixing solutions of sodium chloride and argentous citrate.

Argentic chloride is found native in South America, Siberia, Norway, France, and Cornwall, and constitutes a valuable ore of silver. The *buttermilk ore* of the German miners, found in the Hartz, is a mixture of clay and silver chloride. Silver chloride is readily obtained artificially by adding hydrochloric acid or a chloride to a solution of silver nitrate. It forms a white curdy mass of specific gravity 5·7, and is almost absolutely insoluble in water. It dissolves in about 50,000 parts of nitric acid. It is more readily soluble in strong hydrochloric acid, and in solutions of alkaline chlorides. Ammonia dissolves it readily, forming the compound $3NH_3.2AgCl$, which may be obtained in rhombic crystals by evaporation. It is also readily soluble in sodium thiosulphate solution, forming a double salt of the composition $Ag_2Na_4S_6O_9$, which may be obtained crystallised with 2 molecules of water; it also dissolves in solution of potassium cyanide, forming potassio-argentic cyanide, AgCy.KCy.

Silver chloride melts at about 457°, to a clear yellow liquid which solidifies to a translucent resinoid mass. It is readily reduced to metallic silver by fusion with alkaline carbonates or cyanides, or by heating in a current of hydrogen gas. The metal is also obtained by boiling the chloride with a strong solution of potash, or potassium carbonate and grape sugar.

On exposure to light, silver chloride quickly darkens in colour, becoming at first violet, and ultimately dark-brown or almost black. The change is accompanied by loss of chlorine, and the sub-chloride or argentous chloride is said to be formed.

74. Silver Bromides.—An argentous bromide is supposed to be formed by the action of light upon argentic bromide.

Argentic Bromide, AgBr, is found native, as *bromargyrite*, in Mexico and Chili. It is obtained artificially by mixing solutions of potassium bromide and silver nitrate as a yellowish-white curdy precipitate very slightly soluble in nitric acid, soluble in ammonia, although less readily so than the chloride. It melts at 434°, and is darkened by exposure to light.

The minerals known as *embolite*, *megabromite*, and *microbromite*, found in Chili, are mixtures of silver bromide and chloride.

75. **Silver Iodide,** AgI, is found native in Mexico and in Chili, in hexagonal crystals, or in thin plates of a yellowish-green colour, forming the mineral known as *iodargyrite.* It may be obtained by dissolving silver in strong hydriodic acid, or by mixing solutions of potassium iodide and silver nitrate. It has a light yellow colour which is not preceptibly altered by exposure to light unless it contains silver nitrate, when it assumes a greenish colour. By the addition of nitric acid or solution of potassium iodide the original yellow colour of the precipitate is restored. Argentic iodide is very slightly soluble in acids and in ammonia. It is almost insoluble in solutions of alkaline chlorides, but readily dissolves in a concentrated solution of potassium iodide, forming the compound AgI.KI. Silver iodide is decomposed when heated in a stream of chlorine and when boiled with strong nitric acid. It melts at 530°.

76. **Silver Fluoride,** AgF, is obtained in quadratic octahedrons of specific gravity 5·852, and containing 1 molecule of water, by dissolving the oxide or carbonate in aqueous hydrofluoric acid. It is deliquescent, and is soluble in half its weight of water, forming a strongly alkaline liquid. It is not decomposed by sunlight.

77. **Silver Sulphide,** Ag_2S, is found native as *silver glance,* and is obtained by fusing silver with sulphur, or by passing sulphuretted hydrogen into solutions of silver salts. It is readily fusible, forming when cold a leaden-grey mass, which is so soft that it may be readily cut with a knife and pressed into moulds.

78. **Silver Selenide** is also found native in union with lead selenide, forming the mineral *naumannite,* $PbSe.Ag_2Se$. With copper selenide it forms the mineral *eukairite,* $Ag_2Se.Cu_2Se$.

79. **Silver Telluride,** Ag_2Te, occurs in nature as the mineral *hessite.*

80. **Silver Sulphate,** Ag_2SO_4, is formed by the action of hot concentrated sulphuric acid on the metal, or by adding sulphuric acid to a strong solution of silver nitrate. It is sparingly soluble in water; it forms with ammonia a readily soluble compound $2NH_3.Ag_2SO_4$.

81. **Silver Nitrate,** $AgNO_3$, is one of the most important

salts of silver. It is readily made by dissolving the metal in moderately dilute nitric acid, and concentrating the solution, when it separates out in anhydrous tables belonging to the triclinic system. It dissolves in its own weight of cold water, forming a neutral solution, which is partially reduced by the action of hydrogen with the production of silver and silver nitrite. It is soluble in alcohol and ether. It melts at about 224°; when cast into moulds it constitutes the *lunar caustic* of the surgeon. It rapidly attacks and destroys organic matter, and acts as a violent corrosive poison. It stains the skin, hair, etc., black: an ethereal solution of the nitrate is used as a dye for the hair. The marking ink used for writing on linen, etc., is mainly a solution of silver nitrate and gum arabic in water. By mixing dilute solutions of silver nitrate and aldehyd-ammonia (formed by passing ammoniacal gas into aldehyd) metallic silver is gradually separated, and may be deposited upon glass as a highly lustrous mirror.

82. **Triargentic Phosphate,** Ag_3PO_4, is a light yellow powder, obtained by mixing solutions of silver nitrate and an alkaline orthophosphate. It is almost insoluble in water, but readily dissolves in acids and in ammonia. On exposure to light it turns black; when heated it becomes orange red, and at a high temperature melts.

83. **Silver Carbides.**—Several combinations of carbon and silver are known. The compound Ag_4C is stated to be obtained by fusing silver with lamp-black. The monocarbide, AgC, is a grey powder formed by heating silver pyroracemate.

Silver salts heated on charcoal with sodium carbonate in the reducing area of the non-luminous gas flame yield highly lustrous, white, malleable beads of the metal. In solution the salts give a white curdy precipitate of the chloride when mixed with hydrochloric acid; it is insoluble in nitric acid, but readily soluble in ammonia. Sulphuretted hydrogen gives a precipitate of black silver sulphide, Ag_2S, easily soluble in hot nitric acid.

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84. **Thallium.**—Symbol Tl; atomic weight 203·64.—This element was discovered by Crookes, in 1861, in a residue obtained by distilling impure selenium procured from a deposit

in a sulphuric acid manufactory in the Hartz. On examining this residue by the spectroscope, the presence of the new element was revealed by a brilliant line in the green, whence its name from θαλλος, a green bud. Thallium is widely distributed; it is found in iron and copper pyrites, in blende, in native sulphur, and in lepidolite. It also occurs to the extent of about 18 per cent. in a native selenide of copper and silver termed *crookesite.* It is most profitably extracted from the flue-dust of the pyrites burners. The metal is readily procured from the solution of the sulphate by electrolysis or by the action of zinc, as a spongy crystalline mass, which, by fusion in an atmosphere of coal-gas or under potassium cyanide, is obtained in a coherent form. Thallium has a strong metallic lustre, but it quickly tarnishes by oxidation. Its specific gravity is about 11·8; it is softer even than lead, and forms a bluish streak on paper which gradually fades by oxidation. It fuses at 294°, and may be obtained in well-defined octahedral crystals by slow cooling. It is strongly diamagnetic, and its electric conductivity is about 9, that of silver being 100. Thallium volatilises slightly at a red heat; it boils below a white heat, and may be distilled in a stream of hydrogen gas. In contact with oxygen at a high temperature it burns brilliantly, and is mainly converted into thallic oxide. Both the metal and its salts are highly poisonous.

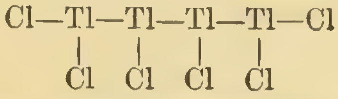
Thallium combines with oxygen in two proportions to form thallous oxide, Tl_2O, and thallic oxide, Tl_2O_3. **Thallous oxide** may be obtained by the action of moist air on the metal. On heating the oxidised mass with hot water the hydrated oxide, $Tl_2H_2O_2$ or TlHO, dissolves and crystallises out, as the solution cools, in pale yellow prisms. The crystals lose their water on heating, and readily melt to a dark-brown liquid which corrodes glass and porcelain. The oxide is easily soluble in water, and forms a strongly alkaline solution resembling that of potash. It attacks the skin, staining it a dark-brown colour. Like potash it precipitates many oxides, *e.g.*, those of lead, iron, cobalt, nickel, mercury, silver, manganese, etc.; it throws down the aluminium and chromium hydrates, but redissolves them when added in excess. By long continued boiling it slowly absorbs oxygen, and is partially converted into the sesquioxide or **thallic oxide,**

Tl_2O_3. This oxide is the chief product of the combustion of the metal in oxygen. It may be obtained by the addition of sodium hypochlorite to a solution of the thallous chloride in sodium carbonate, or by the action of hydrogen dioxide on the metal, or by passing a voltaic current through a neutral solution of thallous sulphate; the metal is formed at the negative pole, and the positive pole gradually becomes coated with a cake of thallic oxide which afterwards slowly dissolves in the free sulphuric acid. On the addition of ammonia, or potash, or thallous hydrate, it is reprecipitated as a brown powder possessing the composition $Tl_2H_2O_4$ or $TlHO_2$. On heating it becomes anhydrous, and at a high temperature evolves oxygen.

85. **Thallium Chlorides.**—The following combinations of chlorine and thallium are known:—Thallium monochloride, $TlCl$; thallium sesquichloride, Tl_4Cl_6; thallium dichloride, Tl_2Cl_4; thallium trichloride, $TlCl_3$. The sesqui- and di-chloride may be represented as combinations of the mono- and trichlorides, thus: $3TlCl.TlCl_3$ and $TlCl.TlCl_3$.

Thallium Monochloride is the first product of the action of chlorine on the metal. It is more readily obtained by the addition of a soluble chloride to a solution of thallous sulphate as a white curdy precipitate, resembling lead chloride; like this salt it dissolves in hot water, but is deposited again as the liquid cools. It fuses at 434° to a yellow liquid, which, on cooling, solidifies to a crystalline mass of specific gravity 7·02; like silver chloride, it is readily reduced to the metal by contact with zinc and dilute sulphuric acid. The monochloride forms double salts with platinum tetrachloride, and with gold trichloride, which resemble those produced by the alkaline chlorides. The **chloroplatinate,** Tl_2PtCl_6, is a yellow crystalline powder which requires nearly 16,000 parts of water at the ordinary temperature for solution; hence it is less soluble than the corresponding salts of cæsium, rubidium, and potassium.

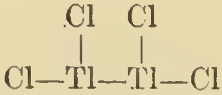
Thallium Sesquichloride, Tl_2Cl_3 or Tl_4Cl_6—



$$\begin{array}{ccccccccc} \mathrm{Cl}- & \mathrm{Tl} & - & \mathrm{Tl} & - & \mathrm{Tl} & - & \mathrm{Tl} & -\mathrm{Cl} \\ & | & & | & & | & & | & \\ & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} & \end{array}$$

is obtained in bright yellow crystalline scales resembling those of lead iodide when the metal or the monochloride is dissolved in warm nitro-hydrochloric acid and the solution cooled. It is even less soluble in cold water than the monochloride. Its solution is decomposed by ammonia into the brown oxide and the monochloride.

The **dichloride**, Tl_2Cl_4—



$$\begin{matrix} & \mathrm{Cl} & \mathrm{Cl} & \\ & | & | & \\ \mathrm{Cl}- & \mathrm{Tl}- & \mathrm{Tl}- & \mathrm{Cl} \end{matrix}$$

is formed by heating the monochloride in chlorine gas; it is a pale yellow crystalline mass which, at a high temperature, is converted into the sesquichloride.

The **trichloride**, $TlCl_3$, is produced by dissolving the trioxide in hydrochloric acid, or by suspending the monochloride in chlorine water. The solution evaporated *in vacuô* yields colourless prisms of the hydrated chloride. It unites with the alkaline chlorides to form double salts, and with ether forms $TlCl_3(C_2H_5)_2O.HCl + H_2O$.

86. **Thallium Monobromide**, TlBr, is a pale yellow powder, nearly insoluble in cold water, and melting at 463°. In contact with bromine it forms the **tribromide**, $TlBr_3$. By partial reduction the tribromide is converted into the **dibromide** Tl_2Br_4, which, by treatment with water, yields the **sesquibromide** Tl_4Br_6.

87. **Thallium Mono-iodide**, TlI, is a bright yellow powder obtained by adding potassium iodide to a solution of thallium sulphate. It is almost insoluble in water, and fuses at 446° to a scarlet liquid. On solidifying, the iodide retains this colour unless the particles are disturbed, when they become yellow—exactly the reverse of that which happens in the case of mercuric iodide. The **tri-iodide** is formed by the action of iodine on the metal in presence of ether. It unites with potassium iodide to form the compound $3KI.2TlI_3$ (Rammelsberg), which forms large crystals belonging to the regular system, of a black colour by reflected light and of a deep red by transmitted light.

88. **Thallium Monofluoride** is a readily soluble salt, obtained by dissolving thallous carbonate in hydrofluoric acid. It volatilises on heating and turns black on exposure to light. The **trifluoride** is a dark-green insoluble powder formed by

the action of strong hydrofluoric acid on the trioxide. The **silicofluoride**, $2TlF.SiF_4.2H_2O$, unlike the corresponding salt of potassium, is readily soluble in water.

89. **Thallium Chlorate**, $TlClO_3$, and **perchlorate**, $TlClO_4$, are anhydrous salts isomorphous with the corresponding potassium compounds, and like those bodies sparingly soluble in cold water.

90. **Thallous Sulphide**, Tl_2S, is obtained of a dark-brown colour by adding ammonium sulphide to a solution of a thallous salt. It is insoluble in excess of the precipitant, but dissolves readily in dilute sulphuric or nitric acid. Sulphuretted hydrogen passed into a strong solution of thallous sulphate, acidulated slightly with sulphuric acid, precipitates the same sulphide in thin crystalline plates of a blue-black colour. No thallic sulphide is known.

91. **Thallous Sulphate**, Tl_2SO_4, is formed by the action of sulphuric acid on the metal or on the nitrate or chloride. It is readily soluble in water, and crystallises in rhombic prisms isomorphous with potassium sulphate. With aluminium sulphate it forms **thallium alum**, $TlAl(SO_4)_2.12H_2O$, isomorphous with ordinary alum; it combines with the sulphates of iron, nickel, and magnesium, to form a series of double salts isomorphous with those produced by potassium sulphate.

Thallic Sulphate, $Tl_2(SO_4)_3.7H_2O$, is an easily decomposable salt formed by dissolving thallic oxide in dilute sulphuric acid.

92. **Thallium Nitrate**, $TlNO_3$, is formed by dissolving the metal in nitric acid. The salt is easily soluble in water, but insoluble in alcohol.

93. **Thallium Phosphates.**—The following salts of thallium and phosphoric acid are known:—

Thallium metaphosphate, $TlPO_3$.

Ortho Salts—

Thallium dihydrogen phosphate, TlH_2PO_4
Dithallium hydrogen phosphate, Tl_2HPO_4
Trithallium phosphate, Tl_3PO_4.

Pyro Salts—

Dithallium dihydrogen pyrophosphate, $Tl_2H_2P_2O_7$
Tetrathallium pyrophosphate, $Tl_4P_2O_7$.

They are colourless salts, and are all more or less soluble in water.

94. Thallium Carbonate, Tl_2CO_3, may be prepared by allowing the metal to oxidise in a damp atmosphere containing carbonic acid. It forms white anhydrous crystals, soluble in water, especially on heating; its solution is caustic and strongly alkaline. On mixing its solution with potassium platino-cyanide, beautiful bronze-green dichroic crystals of the composition $PtTl_2Cy_4.Tl_2CO_3$ are formed.

Thallium may easily be detected by the magnificent green colour which it imparts to the non-luminous flame, which in the spectroscope is seen to yield a single green line. Like lead, it forms a sparingly soluble chloride, but is distinguished from that element by the ready solubility of its sulphate. With platinum tetrachloride it forms the highly insoluble chloroplatinate $PtTl_2Cl_6$.

CHAPTER VI.

GROUP II.—DYAD METALS.

Beryllium.
Magnesium.
Zinc.
Cadmium.

Calcium.
Strontium.
Barium.

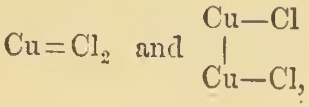
Copper.
Palladium.
Mercury.

These metals are capable of replacing the hydrogen in hydrochloric acid in the proportion of one atom of metal to two atoms of hydrogen to form chlorides of the general formula $\overset{II}{M}Cl_2$, and of an atomic heat 18·6. Beryllium was formerly regarded as analogous to aluminium, hence its oxide was represented as Be_2O_3, and its chloride as Be_2Cl_6, the atomic weight of the element being taken as 13·9. A closer study of its derivatives has made its relationships to the magnesium sub-group more evident, and latterly it has been usual to regard it as a dyad. All doubt as to its true position as a member of the magnesium group has been removed by the determination of its atomic heat by Dr. Emerson Reynolds.

Beryllium, magnesium, zinc, and cadmium, together constitute a family group. The atomic weights of the three last named members show a gradational order similar to that exhibited by sub-groups among the monad metals; the atomic weight of zinc is approximately the mean of that of magnesium and cadmium. The heat of combination of zinc is also midway between that of magnesium and cadmium. The metals of this group are permanent in pure dry air, and are volatile at high temperatures; the volatility of the several members increases with their atomic weights. The vapour densities of zinc and cadmium are only half their atomic weights. The chlorides and sulphates of this group are readily soluble in water; the oxides, hydrates, and carbonates, are practically insoluble. Cadmium sulphide is insoluble in water and in hydrochloric acid; zinc sulphide is insoluble in water, but readily soluble in hydrochloric acid; magnesium sulphide is decomposed even by water; the beryllium compound does not appear to exist.

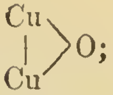
Calcium, strontium, and barium constitute an equally well-defined family of elements; the atomic weight of strontium is nearly equal to the arithmetic mean of the atomic weights of calcium and barium. These metals have a low specific gravity and possess a bright yellow colour; on exposure to air they are rapidly oxidised, and they decompose water with evolution of hydrogen and formation of hydroxides. Calcium sulphate is slightly soluble in water, strontium sulphate is very sparingly soluble, and barium sulphate is practically insoluble. On the other hand, the hydrates and carbonates show the reverse order of solubility—the barium compounds are the most, and the calcium compounds the least, soluble in water; the strontium derivatives in both cases being intermediately soluble.

Copper forms two chlorides—

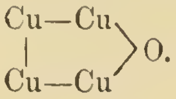


$$Cu{=}Cl_2 \quad \text{and} \quad \begin{array}{l} Cu{-}Cl \\ \;| \\ Cu{-}Cl, \end{array}$$

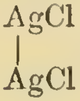
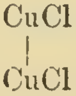
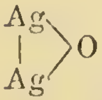
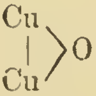
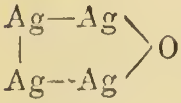
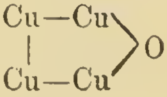
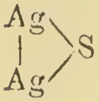
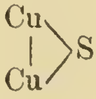
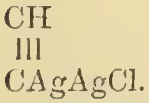
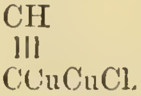
and two stable oxides—

$Cu=O$ and 

in each of these bodies it behaves as a dyad. In the little known quadrantoxide, obtained by Rose by the action of an alkaline solution of stannous oxide upon a cupric salt, the copper may also be assumed to be diadic; thus

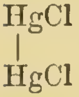


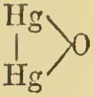
Many cuprous compounds are isomorphous with the corresponding derivatives of silver; hence the two series of bodies may be supposed to have the same constitution. For this reason Wislicenus has been led to regard silver as bivalent, and to formulate argentic compounds as analogous to cuprous compounds; thus—

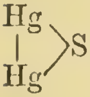
 $\begin{array}{l}AgCl\\ \vert\\ AgCl\end{array}$	Argentic Chloride.	 $\begin{array}{l}CuCl\\ \vert\\ CuCl\end{array}$	Cuprous Chloride.
	Argentic Oxide.		Cuprous Oxide.
	Argentous Oxide.		Copper Quadrant Oxide.
	Argentic Sulphide.		Cuprous Sulphide.
 $\begin{array}{l}CH\\ \vert\vert\vert\\ CAgAgCl.\end{array}$	Ethine Silver Chloride.	 $\begin{array}{l}CH\\ \vert\vert\vert\\ CCuCuCl.\end{array}$	Ethine Cuprous Chloride.

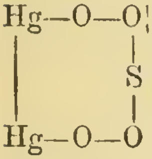
Palladium is usually classed with platinum and its congeners as a tetrad, but in its best-defined compounds it behaves as a dyad; the few palladic compounds which are known are very unstable. The chloride, $PdCl_4$, and the chloro-palladinates are readily decomposed on heating, even in solution, with loss of chlorine; and the dioxide has not been definitely obtained.

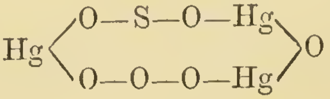
Mercury forms two series of derivatives, known as mercurous and mercuric compounds, comparable to the cuprous and cupric compounds, and represented by similar formulæ:

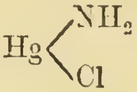

$\begin{matrix}HgCl\\|\\HgCl\end{matrix}$ Mercurous Chloride. $Hg{=}Cl_2$ Mercuric Chloride.


$\left.\begin{matrix}Hg\\|\\Hg\end{matrix}\right\rangle O$ Mercurous Oxide. $Hg{=}O$ Mercuric Oxide.


$\left.\begin{matrix}Hg\\|\\Hg\end{matrix}\right\rangle S$ Mercurous Sulphide. $Hg{=}S$ Mercuric Sulphide.


$\begin{array}{l}Hg-O-O\\ |\qquad\quad\;\; |\\ |\qquad\quad\;\; S\\ |\qquad\quad\;\; |\\ Hg-O-O\end{array}$ Mercurous Sulphate.


$Hg\left\langle\begin{matrix}O-S-O-Hg\\O-O-O-Hg\end{matrix}\right\rangle O$ Turpeth Mineral.


$Hg\left\langle\begin{matrix}NH_2\\Cl\end{matrix}\right.$ White Precipitate.

The vapour density of mercury is only half its atomic weight; in this respect it resembles cadmium and zinc.

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95. **Beryllium** or **Glucinum**—Symbol Be; atomic weight 9·3.—The existence of this element was first demonstrated by Vauquelin in 1798. It is found in *beryl, emerald, euclase,* double silicates of alumina and berylla, and in *helvine,* a silicate of manganese, iron, and beryllium, combined with a manganese oxysulphide; this body is interesting as the only example known of a naturally occurring compound of a silicate and a sulphide. *Phenacite* is a simple silicate of berylla; *chrysoberyl* is a compound of alumina and berylla. Beryllium is a white malleable metal of specific gravity 2·1, resembling aluminium, and obtained by reducing the chloride with sodium. It is susceptible of a high polish, does not tarnish in the air, and resists the action of most oxidising agents. It is incapable of decomposing water even at a white heat, and boiling nitric acid has scarcely any action on it; sulphuric and hydrochloric acids and caustic potash dissolve it with evolution of hydrogen.

96. **Berylla,** BeO, the only known oxide of beryllium, is

a white, bulky powder, insoluble in water, and volatilising, without previous fusion, at a high temperature. It may be obtained in hexagonal prisms, isomorphous with zinc oxide, by long continued fusion with boric acid.

The **hydrate**, BeH_2O_2, is formed by the action of caustic alkalies on solutions of beryllium salts. Like alumina it is soluble in potash or soda, but is precipitated from these solutions on boiling as a dense powder of the formula $3BeH_2O_2.H_2O$. Unlike alumina, it is soluble in a cold solution of ammonium carbonate.

97. **Beryllium Chloride**, $BeCl_2$, is a white deliquescent, fusible, volatile substance, obtained by passing chlorine over a strongly heated mixture of berylla and charcoal. It dissolves in water with considerable rise of temperature, and the solution yields a hydrated chloride on evaporation. **Beryllium chloroplatinate**, $BeCl_2.PtCl_4.9H_2O$, is formed by dissolving berylla in a solution of platinic chloride. A similar compound is known with calcium chloride. Several beryllium sulphates exist, viz., the normal salt, $BeSO_4.4H_2O$, and basic salts, $BeSO_4.BeO_2H_2.2H_2O$ and $Be''SO_4.5BeO_2H_2.2H_2O$, but no alum is known. A *potassium beryllium sulphate* exists, but it cannot be obtained crystallised in octahedra, and it contains only two molecules of water. The ammonium salt has a similar composition.

The reactions of beryllium are very similar to those of aluminium. Compounds of beryllium, however, fail to give a blue colour when heated in the non-luminous flame with cobalt nitrate; moreover, ammonium carbonate dissolves berylla hydrate, whereas alumina remains undissolved. Caustic potash precipitates the hydrate which redissolves in excess of the alkali; on boiling, the precipitate is again formed.

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98. **Magnesium** — Symbol Mg; atomic weight 24·0.— This element, in a state of combination, occurs widely distributed, and is found in a great variety of minerals. It is met with as hydrate, carbonate, chloride, bromide, sulphate, phosphate, and nitrate; it exists in a large number of bodies in combination with silica, as, for example, in *hornblende*, *augite*, *talc*, *anorthite*, *steatite*, *soap-stone*, *asbestus*, etc. It is

found in many mineral waters, as in the springs at Epsom, Harrogate, Cheltenham, etc. Sea-water contains considerable quantities of the chloride and sulphate.

Magnesia was first clearly distinguished from lime by Bergmann and Scheele about the middle of the eighteenth century. The metal was isolated by Davy in 1808, and is now obtained on a considerable scale by heating the anhydrous chloride with sodium, and distilling the crude product. Magnesium possesses a silvery-white colour, and acquires a high lustre by polishing; its specific gravity is 1·74; it fuses at a dull red heat, and may be readily distilled. It is malleable, and may be drawn out into wire, although not of any great thinness. When strongly heated in contact with air it burns with a bright white light, rich in chemically active rays.

99. Magnesium Monoxide, or **Magnesia**, MgO, the only known oxide of the element, is formed when the metal burns in oxygen or in the air, and may be obtained by igniting the carbonate or nitrate. The product formed by heating the carbonate at a low temperature is a bulky, white powder of specific gravity 3·0; by strong ignition it contracts greatly, and acquires a density of 3·6. It is very slightly soluble in water (1 part in 55,000), and the solution has a faint alkaline reaction. The **hydrate**, MgH_2O_2, occurs as the mineral *brucite*: it may be obtained artificially by adding a solution of caustic potash or baryta to a salt of magnesium. It is readily dehydrated on heating.

100. Magnesium Chloride, $MgCl_2$, cannot readily be obtained in the anhydrous state by evaporating its aqueous solution to dryness, as the salt suffers partial decomposition into hydrochloric acid and magnesia. If, however, the solution be mixed with ammonium chloride, a double salt is obtained, which may be rendered anhydrous by evaporation; and if this be strongly heated, the ammonium chloride is expelled, leaving pure anhydrous magnesium chloride. The salt melts at a dull red heat, and solidifies to a translucent mass of flexible plates. It is very deliquescent, and dissolves in water with evolution of heat; a concentrated solution deposits crystals of the composition $MgCl_2.6H_2O$. Magnesium chloride forms double salts with the alkaline chlorides; the potassium compound is obtained on the large scale in the concentration of certain brines; its composition is $KCl.MgCl_2 6H_2O$. The same compound is found in thick layers in the salt-beds of Stassfurth, as *carnallite*, and is used as a source of potassium chloride (see p. 115). Several oxychlorides are known which solidify on hydration like gypsum, and form hard cohesive masses, capable of being polished. The crystalline deposit, which forms in ammoniacal solutions of magnesium salts and sal-ammoniac, so-called "magnesia mixture," has the composition $MgCl_2.5MgO.13H_2O$.

101. Magnesium Bromide, $Mg Br_2$, is found in sea-water and in many mineral springs: it strongly resembles the chloride.

102. Magnesium Sulphate, $MgSO_4$.—This important salt occurs in sea-water and in many mineral springs. It is occasionally met with in nature crystallised, constituting the mineral known as *Epsomite* or *hair salt:* it occurs in compact masses, as *Reichardite*, in the Stassfurth salt mines. It is prepared on the large scale by calcining dolomite, washing the mass with water, to remove the greater portion of the more soluble lime, and treating the residue with dilute sulphuric acid, which dissolves out the magnesia. By crystallization the magnesium sulphate is readily obtained pure. It is soluble in about its own weight of water at ordinary temperatures. As usually procured it contains 7 molecules of water, 6 of which are expelled on heating to 150°: the heptahydrated salt is isomorphous with the corresponding sulphates of zinc and nickel, and with magnesium chromate. Fig. 121 represents one of its most characteristic forms. Occasionally a strong solution deposits the heptahydrated salt in monoclinic prisms. If a concentrated solution be left to crystallise at 30°, the hexhydrated salt $MgSO_4.6H_2O$ is obtained in monoclinic crystals; a monohydrated salt, $MgSO_4.H_2O$, occurs as a natural product in the so-called *abraum salz* of the Stassfurth potash works, and is known as *kieserite*. It is used in wool-washing and in the manufacture of "permanent white" by precipitation with barium chloride. A number of compounds of magnesium and

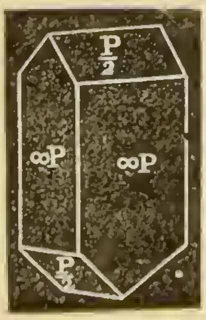


Fig. 121.

alkaline sulphates may be obtained, which generally contain 6 molecules of water of crystallization. They may be regarded as derived from the heptahydrated salt by the substitution of a molecule of the alkaline sulphate for the molecule of the water of constitution, *i.e.*, that which is retained on drying the salt at 150° (see Vol. I., p. 113). The potassium salt $K_2SO_4MgSO_4.6H_2O$ is obtained in the concentration of brine from sea-water. An analogous sodium salt with 4 molecules of water is found in the Stassfurth salt-beds, and is known as *astracanite.* Magnesium sulphate also crystallises with the other isomorphous heptahydrated salts, forming so-called *composite* or *coupled salts.* The magnesium-ferrous sulphate has the formula $MgFe(SO_4)_2.14H_2O$. A potassium calcium-magnesium-sulphate, $MgCa_2K_2(SO_4)_4.2H_2O$, is found native, and is known as *polyhalite.*

103. **Magnesium Nitrate,** $Mg(NO_3)_2$, is occasionally found in well waters, and is readily procured by dissolving the oxide or carbonate in nitric acid and evaporating. It is readily soluble in water and alcohol, and may be obtained from its solutions crystallised with 6 molecules of water or of alcohol.

104. **Trimagnesium Orthophosphate,** $Mg_3P_2O_8$, is an important constituent of the inorganic portion of many plants and seeds, as for example of the grain of wheat. It is also found in the bones of animals and in certain animal concretions. Ammonium-dimagnesium orthophosphate, $(NH_4)_2Mg_2P_2O_8.12H_2O$, is formed by mixing ordinary sodium phosphate with magnesium salts containing ammonium chloride and ammonia. When precipitated from dilute solutions the salt is obtained crystalline: it is highly insoluble in water containing ammonia. This salt constitutes the so-called fusible calculus; it is deposited from putrefying urine, and is occasionally met with in guano. When ignited it parts with ammonia and water, and is converted into **magnesium pyrophosphate,** $Mg_2P_2O_7$.

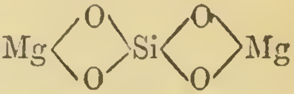
105. **Magnesium Carbonate,** $MgCO_3$, occurs native in rhombohedral crystals, as *talc-spar.* It may be obtained artificially by mixing solutions of sodium carbonate and magnesium sulphate or chloride, and treating the precipitate with carbonic acid. The magnesium carbonate dissolves, and on evaporating the solution the salt is obtained

in minute crystals isomorphous with those of aragonite. By conducting the evaporation at different temperatures various hydrated carbonates may be formed. The *magnesia alba* of the shops is a mixture of the carbonate and hydrate, prepared by mixing solutions of Epsom salts (magnesium sulphate) and sodium or potassium carbonates. The relative proportion of the hydrate and carbonate varies with the strength of the solutions and the temperature at which the mixture is made. A basic carbonate of the composition $Mg(HO)_2.3(MgCO_3.H_2O)$ is found native as *hydro-magnesite*.

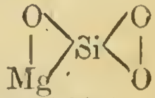
Dolomite is a mixture of magnesium and calcium carbonates. It is exceedingly abundant, many mountain ranges being composed almost exclusively of it. It is used as a source of magnesium compounds. If finely-powdered dolomite be heated to redness in a closed space the magnesium carbonate is decomposed and carbon dioxide is expelled. If the residue be then treated with carbon dioxide under pressure, magnesium carbonate goes into solution, very little of the calcium carbonate being dissolved : on boiling the clarified solution the magnesium carbonate is deposited. A still simpler process consists in treating the finely-ground dolomite with an aqueous solution of carbonic acid in a horizontal rotating cylinder and under a pressure of 5 or 6 atmospheres. The solution, after standing, is run into a vertical cylinder and treated with steam, whereby the magnesium carbonate is precipitated.

106. Magnesium Silicates.—A number of these bodies occur naturally and constitute important minerals. The following are among the best known :—

Dimagnesium Silicate or *Olivin*, (*peridote*), } Mg_2SiO_4 or



Monomagnesium Silicate or *Augite*, (*enstatite*), $MgSiO_3$ or



Trimagnesium Tetrahydrogen Trisilicate or *Serpentine*, $Mg_3H_4Si_3O_9$
Dimagnesium Tetrahydrogen Trisilicate or *Meerschaum*, $Mg_2H_4Si_3O_9$
Trimagnesium Tetrasilicate or *Steatite*, $Mg_3Si_4O_{12}$
Tetramagnesium Pentasilicate or *Talc*, $Mg_4Si_5O_{15}$

Compounds of magnesium heated with cobalt nitrate in the non-luminous Bunsen flame yield a rose or flesh-coloured mass. In solution they afford no precipitate with sulphuretted hydrogen or ammonium sulphide; with the fixed alkalies or their carbonates they yield a precipitate of the hydrate or carbonate soluble in ammonium chloride solution. Lime or baryta-water precipitate magnesium hydrate. Sodium phosphate yields magnesium phosphate; in presence of ammonia magnesium ammonium phosphate, $MgNH_4PO_4$ is formed.

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107. Calcium—Symbol Ca; atomic weight 40.—Compounds of this element are very abundant and are widely distributed: among them may be enumerated the carbonate which exists as *chalk*, *limestone*, *marble*, *calc-spar*, etc.; the sulphate as *gypsum* and *selenite;* the fluoride as *fluor-spar;* and the phosphate as *apatite* and *bone earth*. The metal was first isolated by Davy. It is best obtained by heating calcium iodide with sodium in a covered iron crucible, or by electrolysing a fused mixture of calcium and strontium chlorides containing ammonium chloride. It is a yellow metal of specific gravity 1·58, somewhat resembling gold in colour; like that metal it is very ductile and malleable; it gradually tarnishes even in dry air, and is quickly oxidised in presence of moisture; it decomposes water with rapidity with the evolution of hydrogen gas and the formation of calcium hydrate. Strong nitric acid has no action upon it in the cold, but the diluted acid dissolves it readily.

108. Calcium Monoxide or **Lime**, CaO.—This compound is best obtained, when required pure, by strongly igniting the artificial carbonate, made by mixing solutions of calcium chloride or nitrate with ammonium carbonate. It may also be made by strongly heating pure marble. The complete expulsion of the carbon dioxide requires a long-continued heat; it is more readily accomplished by passing steam, or a current of air, over the ignited substance. Lime, when pure, is perfectly white and infusible. When strongly heated it emits a bright white light; advantage is taken of this property in the oxyhydrogen light. On exposure to moist air it gradually crumbles to powder, from absorption of water and conversion into the hydrate CaH_2O_2. When moistened with water it evolves great heat, from the formation of the same hydrate; by exposure to a red heat the water is expelled and the monoxide is again formed. The hydrate is soluble in water, although not to the same extent as the hydrates of barium and strontium. Its solubility diminishes with the increase of temperature, so that a cold saturated solution becomes turbid on boiling; on cooling the precipitate is redissolved. It is probable that this phenomenon is due to changes in the hydration of the substance. The solution of calcium hydrate (lime-water) rapidly absorbs carbonic acid from the air, and becomes turbid from the formation of calcium carbonate.

Lime is obtained on the large scale by roasting masses of limestone in kilns, in which the limestone is introduced at the top, and when calcined is allowed to fall out at the bottom, the expulsion of the carbon dioxide being effected by the heat of a fire placed at the side of the furnace. Lime is principally used for making *cements* and *mortars*. *Mortar* is prepared by thoroughly mixing slaked lime, made into a paste with water, with three or four times its weight of clean sharp sand. The sand is added to give cohesion to the mass and prevent shrinkage, since the hydrate when dry is apt to fall to pieces. The character of the mortar depends greatly upon the lime used. A limestone containing much magnesium or aluminium silicate yields what is technically known as *poor* lime; such lime slakes slowly and evolves little heat on hydration. The smaller the amount of impurity in the lime the more rapidly does it slake, and the greater is the rise of temperature accompanying its hydration. Siliceous limestones require great care in burning, otherwise the calcium silicate which is formed partially fuses and the surface becomes vitrified, so that hydration takes place but slowly; such lime is said to be *dead-burnt*. The hardening of mortar is due to several causes, viz., to the drying of the mass, to the conversion of a portion of the lime into carbonate by absorption of atmospheric carbonic acid, and to the formation of a hydrated calcium silicate by the union of the lime with the silica of the sand. The conversion of the free lime into carbonate is never complete, even after the lapse of very long periods of time. Mortar taken from the Pyramids has been found to contain a considerable quantity of uncombined lime.

Ordinary mortar cannot be used for structures which are in continual contact with water, such as breakwaters, quays, piers of bridges, etc., as it is apt to soften and become disintegrated in consequence of the gradual dissolving away of the lime. Certain argillaceous limestones are found to yield lime which hardens under water and resists its solvent action completely. *Hydraulic mortar* is made by calcining a mixture of levigated chalk and clay at a moderately high temperature. *Portland cement* is prepared in this manner. *Roman cement* is a hydraulic mortar containing about 30 per cent. of clay. *Puzzuolana* is a volcanic product composed of silicates of alumina, lime, and alkalies, found at Puzzuoli, near Naples; it is also obtained from the Apennines, and in the neighbourhood of Rome. When ground and mixed with lime it forms a hydraulic mortar of great value; this mixture was employed by the Romans in the construction of many of their buildings. Hydraulic mortars are essentially basic silicates of lime and magnesia, and they "set" by virtue of their power of absorbing and combining with water. In the act of hydration no very considerable rise of temperature is observed, nor does the mass increase much in bulk; the rapidity with which it sets depends upon the proportion of clay which it contains.

Lime is used to a considerable extent in agriculture. It assists in the disintegration of soil and promotes the decomposition of peaty matter. It is employed in many manufacturing operations, *e.g.*, in removing the hair from hides preparatory to their being tanned, in the purification of coal-gas, in the manufacture of bleaching powder, etc.

109. Calcium Dioxide, CaO_2, unlike the corresponding barium compound, cannot be obtained by heating the monoxide in oxygen gas. The hydrated dioxide, $CaO_2.8H_2O$, may be prepared by adding lime-water to a solution of hydrogen dioxide. It is permanent when dry; when heated to 100°, it is converted into the anhydrous dioxide, which is a pale buff-coloured powder, very sparingly soluble in water.

110. Calcium Chloride, $CaCl_2$, has been found to occur at Guy's Cliffe in Warwickshire, and exists in many mineral waters. It is easily made by the action of hydrochloric acid on marble or chalk, and is thus obtained as a bye-product in the manufacture of carbon dioxide (Vol. I., p. 239). It is also formed in preparing ammonia from lime and sal-ammoniac. A concentrated solution of the chloride deposits crystals containing six molecules of water. On redissolving this hydrate in water, great cold results; when mixed with snow the temperature sinks to – 40°. When heated to 200° it forms a porous mass which is exceedingly hygroscopic, and is of great use in drying gases and in dehydrating certain liquids. It fuses at 723°; it combines with ammonia gas, and dissolves readily in alcohol, forming a crystalline compound.

111. **Calcium Fluoride** or **Fluor-spar,** CaF_2, occurs in well-defined cubical or octahedral crystals of various colours, accompanying lead ores in Cornwall, Cumberland, and Derbyshire. It is found in bones and teeth, and is present in more or less quantity in many minerals, such as *tourmaline, topaz, fluor-apatite,* etc. Many varieties of the fluor-spar, when gently heated, become phosphorescent. When strongly heated the fluoride melts; whence its application as a flux in smelting metals; hence, too, its name of fluor-spar. When heated with strong sulphuric acid it yields hydrofluoric acid; this mineral, indeed, affords the main source of the acid.

112. **Calcium Sulphides.**—The **monosulphide,** CaS, is a white amorphous sparingly soluble substance formed by the reduction of the sulphate with charcoal, or by heating lime in a current of sulphuretted hydrogen. When heated it shines in the dark; hence its old name of *Canton's phosphorus.* The **disulphide,** CaS_2, is obtained crystallised with three molecules of water by boiling milk of lime with sulphur. If an excess of sulphur be taken, and the boiling be long continued, the **pentasulphide** CaS_5 is formed. The **sulphydrate** CaH_2S_2 may be procured by passing sulphuretted hydrogen into milk of lime. It is permanent only in solution. An **oxysulphide,** 2CaS.CaO, is contained in recently lixiviated "soda waste." Orange-coloured acicular crystals of the composition $4CaO.CaSO_4,18H_2O$ sometimes separate out by long standing from the oxidised liquors in the sulphur recovery process; similar crystals may be obtained by treating milk of lime with sulphuretted hydrogen, filtering and allowing the solution to stand in an air-tight vessel.

113. **Calcium Sulphate,** $CaSO_4$, occurs naturally as *anhy-*

drite; combined with two molecules of water it constitutes the mineral *selenite.* *Gypsum* and *alabaster* are varieties of calcium sulphate. This salt is frequently found in well and in river waters; such waters are not softened by boiling, and, accordingly, are said to be "permanently hard." When used for generating steam they occasionally deposit the sulphate on the sides of the boiler as a hard coherent crust, the formation of which is facilitated by the circumstance that the salt is less soluble in boiling water than in water at common temperatures. At about 200° the sulphate parts with its water of crystallization and forms a friable mass which, when powdered, constitutes *plaster of Paris.* The dried sulphate, when made into a paste with water, gradually solidifies, from the combination of the water, to form the hydrated salt; in the act of hydration a considerable rise of temperature is observed. If the sulphate be heated much beyond 200° it contracts and loses the power of setting when mixed with water, but if small quantities of potassium sulphate, or alum, or borax, be added to it, it may be heated nearly to redness without loss of this property. The mixture sets slowly, but it ultimately becomes very hard, and is susceptible of a high polish.

114. Calcium Nitrate, $Ca2NO_3.4H_2O$, is a highly deliquescent salt, readily soluble in alcohol. It is occasionally found in natural waters, and is produced in the decomposition of nitrogenous organic matter in presence of lime or its carbonate.

115. Calcium Phosphide, Ca_xP_x, is formed by passing vapour of phosphorus over strongly heated lime. It is a reddish brown substance which, when thrown into water, evolves spontaneously-inflammable hydrogen phosphide (Vol. I., p. 369).

116. Calcium Phosphates.—The **monometaphosphate** CaP_2O_6 is an insoluble white powder obtained by dissolving calcium carbonate in orthophosphoric acid, evaporating, and heating the residue to 320°. The **dimetaphosphate** $Ca_2P_4O_{12}.4H_2O$ may be obtained crystallised by mixing solutions of the corresponding sodium salt and calcium chloride.

Monocalcium orthophosphate, $CaH_4P_2O_8$, may be obtained in thin crystalline scales containing one molecule of water by concentrating a solution of the tricalcium salt in nitric or hydrochloric acid. It has an acid reaction and is readily soluble in water. The salt melts when heated and is converted into the insoluble metaphosphate. The superphosphate of lime of commerce, which is used extensively as a manure, is a mixture of monocalcium phosphate and calcium sulphate obtained by treating ground bones with oil of vitriol.

A **dicalcium orthophosphate** of the composition $Ca_2H_2P_2O_8.4H_2O$, is found in certain concretions met with in the ureters and cloaca of the sturgeon. It has been found in guano, and may be obtained artificially by mixing dilute solutions of calcium chloride and sodium phosphate and passing carbon dioxide into the liquid: the filtered liquid gradually deposits the salt in rhombic plates.

Tricalcium orthophosphate, $Ca_3P_2O_8$, is the best known and most important member of the series. It is the principal constituent of the inorganic portion of bones; it occurs also in apatite, $3Ca_3P_2O_8.CaF_2$, and constitutes the greater portion of the remarkable concretions known as "coprolites." It may be formed artificially by adding a solution of ordinary sodium phosphate mixed with ammonia to a solution of calcium chloride. It is thus obtained as a gelatinous precipitate which shrinks greatly on drying. It may be procured crystallised by heating dicalcium pyrophosphate with water under pressure. It is insoluble in pure water and dissolves slightly in water containing carbonic acid or sodium chloride. It is readily soluble in concentrated nitric and hydrochloric acids, and is decomposed by strong sulphuric acid.

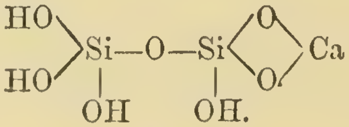
117. Calcium Carbonate, $CaCO_3$, forms a considerable portion of the earth's crust, many mountain chains being made up of this mineral, either alone or associated with magnesium carbonate. The various forms of calc-spar, chalk, and marble consist of calcium carbonate: it is the chief constituent of the shells of birds' eggs, the shells of molluscs, and of coral, and it is found in bones together with calcium phosphate and fluoride. Lime water exposed to the air gradually absorbs carbon dioxide and insoluble calcium carbonate is formed. Carbon dioxide acts very slowly on dry lime. No substance assumes so many varieties of crystalline shape as calc-spar; but the primary form is that of the rhomb into which all the others may be resolved by cleavage. It is also formed in six-sided prisms, constituting the mineral known as *aragonite:* in this form it is isomorphous with *strontianite.* Calc-spar has a specific gravity of about 2·7; the specific gravity of aragonite is about 3·0. When a hot solution of a calcium salt is mixed with an alkaline carbonate calcium carbonate is precipitated in minute crystals having the form of aragonite; if the solutions be cold the crystals take the form of calc-spar. The crystals of aragonite gradually change into those of calc-spar, especially if they be left in the cold liquid. Calcium carbonate is almost insoluble in water, one part of the salt requiring about 10,000 parts of cold water for solution. It is much more soluble in solutions of carbonic acid, but is re-precipitated on boiling the liquid, from the expulsion of the carbon dioxide. When heated, calcium carbonate parts with its carbon dioxide, but the complete expulsion of this gas requires a long-continued heat. If the carbonate be heated in closed vessels it fuses without loss of carbon dioxide, forming on cooling a crystalline mass resembling marble.

The greater number of natural waters contain more or less calcium carbonate held in solution by carbonic acid. By the gradual expulsion of this gas the carbonate is deposited in the form of calc-spar, occasionally combined with 5 molecules of water (Rammelsberg: Salm-Horstmar.) Rain water percolating through limestone rocks dissolves the carbonate. If in its downward passage the solution falls from the roof of a cavern, dependent masses of carbonate are formed termed *stalactites,* owing to the diffusion of the carbon dioxide. If, as usually happens, the solution still retains a portion of the gas the remainder of the calcium carbonate is deposited on the floor on which the water drops; a column of the carbonate is thus formed underneath the stalactite, termed a *stalagmite;* in process of time the two masses meet and a continuous column is produced. *Tufa* is a porous calcareous deposit of similar origin, found in volcanic districts: *travertine* is a more compact variety of the same material.

The hardness of many natural waters is in great part due to dissolved calcium carbonate. On boiling, the chalk is deposited owing to the escape of the carbon dioxide; such waters are said to be "temporarily hard." The deposition of this carbonate on the sides of steam boilers is frequently a great inconvenience, owing to the low thermal conductivity of the cake or coherent deposit. Many plans have been devised for obviating or abating the evil. One of the most efficacious consists in adding a small quantity of sal-ammoniac to the water. Calcium chloride and ammonium carbonate are formed by double decomposition; the former, being a highly soluble salt, remains in solution, the latter is volatile and escapes with the steam. In the other methods the deposit is prevented from becoming coherent: the carbonate is precipitated, but it either remains in suspension or falls down as a loosely aggregated powder. It has been noticed that the latter result may be produced by throwing a few scraps of zinc into the water.

"Temporarily hard" water may be softened by "liming," that is, by adding lime to the water in sufficient quantity to combine with the dissolved carbon dioxide. The mode in which calcium carbonate is held in solution in natural water, and the method of softening it by the addition of lime, were first indicated by Cavendish.

118. Calcium Silicates.—The **monosilicate** or **metasilicate** $CaSiO_3$ occurs native as *tabular-spar* or *Wollastonite* in monoclinic crystals; it may be obtained artificially by mixing solutions of calcium chloride and sodium silicate. *Okenite* is a naturally-occurring **calcium tetrahydrogen disilicate**, $CaH_4Si_2O_7$, or



Diopside is a **calcium magnesium disilicate**, $CaMgSi_2O_6$.

Most compounds of calcium, especially when moistened with hydrochloric acid, impart an orange-red colour to the non-luminous gas flame, which, in the spectroscope, affords characteristic lines in the green and a bright line in the orange.

Sulphuretted hydrogen or the alkaline sulphides give no precipitate with solutions of calcium salts. The normal alkaline carbonates afford a white precipitate of calcium carbonate; the acid carbonates give no precipitate until the solutions are boiled; ammonium oxalate yields calcium oxalate, practically insoluble in water and in dilute acetic acid, readily soluble in nitric or hydrochloric acids. Hydrofluosilicic acid and potassium chromate give no precipitates.

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119. Strontium.—Symbol Sr; atomic weight 87·5.—This element derives its name from Strontian, in Argyleshire, where the carbonate was first discovered. The existence of the new element was indicated by Hope in 1793. Its principal naturally-occurring compounds are the sulphate or *cœlestin*, and the carbonate or *strontianite.* The metal, which was first isolated in an impure state by Davy in 1808, has a yellow colour; its specific gravity is about 2·5; it is rapidly oxidised on exposure to air, and decomposes water with evolution of hydrogen and formation of the hydrate.

The **monoxide**, SrO, is a white infusible powder, obtained by igniting the nitrate or carbonate. It slakes with water and forms the **hydrate** SrH_2O_2. Strontium hydrate dissolves in 2½ parts of boiling water, and in about 50 parts of cold water; its solution deposits crystals of the composition $SrH_2O_2.8H_2O$. The **dioxide**, SrO_2, cannot be formed by heating the monoxide in oxygen; it may be obtained crystallised with eight or twelve molecules of water by mixing solutions of a strontium salt and sodium peroxide. At 100° the crystallised hydrate parts with its water; the dehydrated dioxide is thus obtained as a white powder almost insoluble in water.

120. Strontium Chloride, $SrCl_2.6H_2O$, is formed by dissolving the carbonate in hydrochloric acid, or by converting the sulphate into sulphide by reduction, and treating the reduced mass with hydrochloric acid. It is readily soluble in water and alcohol. Its solution in the latter liquid burns with a red flame. It fuses at 829°.

121. Strontium Sulphate, $SrSO_4$.—Crystals of this compound resembling those of cœlestin may be formed by fusing potassium sulphate with strontium chloride. It is obtained as a white powder by adding sulphuric acid to a solution of a strontium salt. It is very sparingly soluble in cold water, and still less soluble in hot water; 1 part of the salt requires about 7000 parts of cold water, and 9600 parts of boiling water for solution.

The sulphides and sulphydrates resemble the corresponding barium compounds.

122. **Strontium Nitrate,** $Sr2NO_3$, resembles the barium salt. It may be obtained crystallised with four molecules of water; unlike the corresponding lime salt it is nearly insoluble in alcohol. It is principally used in the manufacture of *red fire,* which is a mixture of the dried salt, flowers of sulphur, potassium chlorate, charcoal, and antimony sulphide.

123. **Strontium Carbonate,** $SrCO_3$.—Strontianite is isomorphous with witherite and aragonite. As artificially prepared, by the addition of a solution of an alkaline carbonate to a solution of a strontium salt, it is a white powder almost insoluble in water, but soluble to some extent in solutions of carbonic acid.

Salts of strontium colour the Bunsen flame a beautiful carmine red, which, on examination by the spectroscope, affords a somewhat complicated spectrum containing a characteristic blue line between F and G, and a red line nearly coincident with C. Solutions of strontium salts yield the sparingly-soluble strontium sulphate on the addition of dilute sulphuric acid; they give no precipitate with acid potassium chromate or silicofluoric acid; by the latter reactions strontium may be distinguished from barium. Strontium salts are not precipitated by sulphuretted hydrogen or alkaline sulphides; with ammonium carbonate they yield strontium carbonate.

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124. **Barium**—Symbol Ba; atomic weight 137·2.—Baryta, the monoxide of this element, was first recognised as distinct from lime by Scheele, in 1774. The principal naturally-occurring compounds of barium are the sulphate or *heavy-spar,* and the carbonate or *witherite;* barium salts are found in certain mineral waters, *e.g.*, those of Harrogate. The metal was isolated by Sir H. Davy in 1808. It has a yellow

colour, is readily fusible, has a specific gravity of 4·0, oxidises on exposure to air, and decomposes water with rapidity.

125. **Barium Monoxide**, BaO, is obtained by strongly heating barium nitrate or carbonate. It is a greyish-white powder of specific gravity 5·4; it is strongly alkaline, and is highly poisonous. When heated in the vapour of sulphur trioxide, it forms barium sulphate, $BaSO_4$. It dissolves in water, forming **barium hydrate**, which, by concentration of the solution, is obtained in transparent colourless crystals of the composition $BaH_2O_2.8H_2O$. The solution is highly caustic, and rapidly absorbs carbonic acid from the air. When heated in the air, or in oxygen, it loses water and is converted into the **dioxide** BaO_2. This compound is a greyish-coloured fusible powder, which, when strongly heated, parts with half its oxygen, and forms the monoxide.

This alternate formation and decomposition of the dioxide has been proposed as a means of obtaining oxygen from the air. Air freed from carbon dioxide is passed over moderately heated barium monoxide, which is thereby converted into the dioxide; on raising the temperature the dioxide parts with oxygen, and the monoxide is regenerated. The evolution of the oxygen is facilitated by passing steam over the heated dioxide.

Barium dioxide readily parts with its oxygen when warmed with strong sulphuric acid; if the temperature does not exceed 60° or 70°, a portion of the oxygen is evolved as ozone. When the dioxide is mixed with acidulated water hydrogen dioxide is formed (Vol. I., p. 144), if certain oxides, *e.g.*, those of silver, manganese, lead, etc., be added to the liquid, oxygen is formed, and the oxides are reduced.

126. **Barium Chloride**, $BaCl_2$, is obtained by dissolving the native carbonate in hydrochloric acid, or on a large scale by heating a mixture of barium sulphate and calcium chloride,

$$BaSO_4 + CaCl_2 = BaCl_2 + CaSO_4.$$

By treating the fused mass with hot water, and filtering rapidly, the barium chloride may be easily separated from the sparingly-soluble calcium sulphate. Barium chloride crystallises with 2 molecules of water; it has a bitter taste, and is highly poisonous. It dissolves in about 3 parts of water at 0°, and in about twice its weight at ordinary temperatures.

127. **Barium Sulphide**, BaS, is formed by heating the monoxide in sulphuretted hydrogen gas or in the vapour of carbon bisulphide, or by igniting the sulphate in a stream of hydrogen, or by heating the sulphate with one-third of its weight of bituminous coal. A mixture of the sulphide and the sulphate, obtained by heating the latter substance with an insufficient quantity of carbonaceous matter, is known as the *Bolognian phosphorus*, from its power of shining in the dark after exposure to the sun's rays. Barium sulphide is a white powder, readily soluble in water with formation of the hydrate and sulphydrate—

$$2BaS + 2H_2O = BaH_2O_2 + BaH_2S_2.$$

128. **Barium Sulphate**, $BaSO_4$, occurs in nature as the mineral *heavy-spar* or *barytes* (βαρυς, heavy: in allusion to its high specific gravity), and is readily formed by adding sulphuric acid or a soluble sulphate to solutions of barium salts. It is almost insoluble in water and in dilute acids. When concentrated, the mineral acids take up larger quantities. The solution in sulphuric acid yields an acid salt, $BaH_2 (SO_4)_2$,which is decomposed on the addition of water. Barium sulphate is used to some extent as a pigment under the name of *permanent white.*

129. **Barium Nitrate**, $Ba2NO_3$, may be formed by dissolving witherite in nitric acid, or by heating together solutions of sodium nitrate and barium chloride. The salt dissolves in about twelve parts of water at ordinary temperatures: it crystallises in regular octahedrons. When moderately heated it melts, and at a high temperature it is decomposed with formation of barium monoxide.

130. **Barium Carbonate**, $BaCO_3$, is found native as *witherite*, and may be prepared by mixing solutions of an alkaline carbonate and barium chloride or nitrate. Although almost insoluble in water, it is very poisonous. It may be heated to redness without decomposition, but in presence of vapour of water, or by the addition of charcoal or lime it readily parts with carbon dioxide.

Barium compounds give a greenish-yellow colour to the

Bunsen flame. On examining the light by the spectroscope, it is seen to afford a complicated spectrum consisting of four well-defined lines in the green, three in the yellow, and a broad band in the orange.

Solutions of barium salts give no precipitates with sulphuretted hydrogen, ammonium sulphide, or ammonia; ammonium carbonate throws down barium carbonate; ammonium oxalate yields barium oxalate, sparingly soluble in water and in acetic acid. Solutions of calcium or strontium sulphates give a white precipitate of barium sulphate, almost insoluble in hydrochloric acid, slightly soluble in nitric acid. Hydrofluosilicic acid gives a crystalline precipitate of barium silicofluoride, $BaSiF_6$, sparingly soluble in water; potassium chromate, especially with the acetate, gives a yellow precipitate of barium chromate, $BaCrO_4$.

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131. **Copper.**—Symbol Cu (*Cuprum*); atomic weight 63·4.—Copper has been known from very early times, and was used for the manufacture of tools and weapons long before the discovery of methods for the extraction of iron. The island of Cyprus formerly furnished large supplies of the metal, hence its name of *Œs Cyprium*, or the *Cyprian bronze*, by which it was known to the Romans; this was ultimately shortened to *cuprum*, from which is derived the name by which the metal is now known to us. By the alchemists it was designated by the symbol of the planet Venus ♀. Copper is found native in rhombic dodecahedrons, in filiform pieces, or in thin laminæ in many parts of Wales, Cornwall, in Siberia and in South America; and in large masses in the neighbourhood of Lake Superior. The principal ores of the metal are the *red* and *black oxides*, found in Cornwall, Cuba, South America, and Australia; the *green* and *blue carbonates* found in Siberia, South Australia, and in North and South America: *copper pyrites* or *yellow ore* found in quantity in Devon and Cornwall, Saxony, Sweden, Siberia, Cuba, and Australia; *grey ore*, a mixture of sulphides of copper, iron, arsenic, and antimony, occurring in Cornwall and Saxony. A hydrated silicate known as *chrysocolla* and a hydrated oxychloride, termed *atacamite*, are occasionally employed as ores.

The chief seat of the copper smelting industry in this country is in South Wales, more particularly in the neighbourhood of Swansea. Ores from all parts of the world are here smelted, the different varieties being mixed, or added at various stages of the smelting, so as to facilitate the extraction of the metal. The ore is first calcined in a reverberatory furnace (fig. 122), the materials being so mixed that

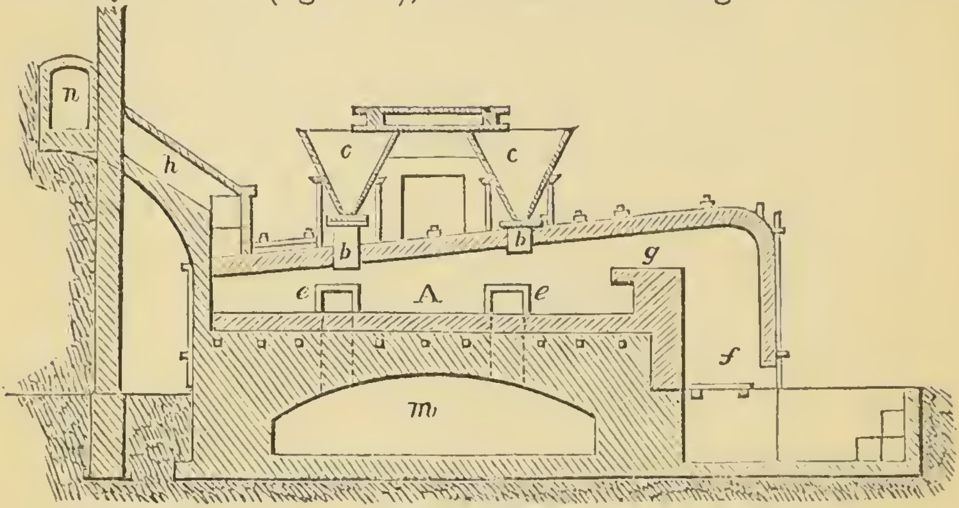


Fig. 122.

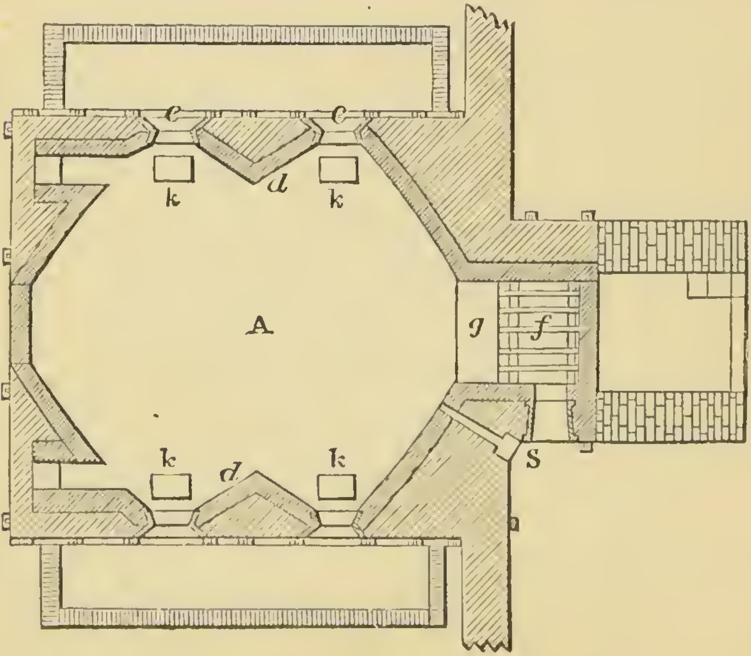


Fig. 123.

the charge of about three tons of sorted ore contains from eight to twelve per cent. of copper. It is introduced by means of the *hoppers, c c* (which are closed during the roasting with fire-clay tiles), and is spread evenly over the fire-brick hearth. It is heated gradually by the reverberating flame from the fireplace, and is stirred from time to time by rakes introduced through the doors, *e e;* a large proportion of the sulphur and arsenic are thus expelled as oxides; a certain portion of the iron becomes converted into ferric oxide, and at the same time suboxide of copper is formed in small quantity. In from twelve to twenty-four hours the charge is raked through the holes *k k*, which are closed by tiles during the roasting, into the chamber *m*, in which it is cooled by throwing water on it. The fuel mainly used is anthracite mixed with bituminous coal: the heat afforded by the combustion is so intense that it is necessary to protect the fire-bars by coating them with fused coal-ash or *clinker*. Carbon dioxide is first formed by union of the oxygen of the air with the carbon of the fuel: in contact with the incandescent coal an additional quantity of carbon is taken up, with the production of carbon monoxide, which ignites at the surface of the mass of fuel, yielding a large spreading flame. Other forms of furnaces are in use, some of which permit of a separation of the products of combustion from the sulphur dioxide, so that the latter gas can be used for the manufacture of sulphuric acid.

The calcined ore is next melted with what is known as *metal-slag*, a silicate of iron containing small quantities of copper, obtained in a subsequent stage of the smelting process, and, of course, from a previous operation. Figs. 124 and 125 represent the *melting* or *ore furnace*, the hearth of which is composed of a mixture of sand and slag cemented together by fusion. The charges of calcined ore, mixed with a small quantity of *raw ore*, consisting of carbonates or oxides of copper, and containing more or less silica as quartz, are introduced through the hopper *c*, and the metal slag is thrown in at the opening *f* at the back of the furnace. After heating for about five hours the whole mass becomes molten, when it separates into two layers, the upper one of which consists of a slag of silicate of iron (*ore-furnace slag*), and the lower one of an impure copper sulphide or *matt* of *coarse metal.* The slag is drawn off through *f*, and the regulus of copper sulphide is run out through the tap-hole *h* into an iron box, with

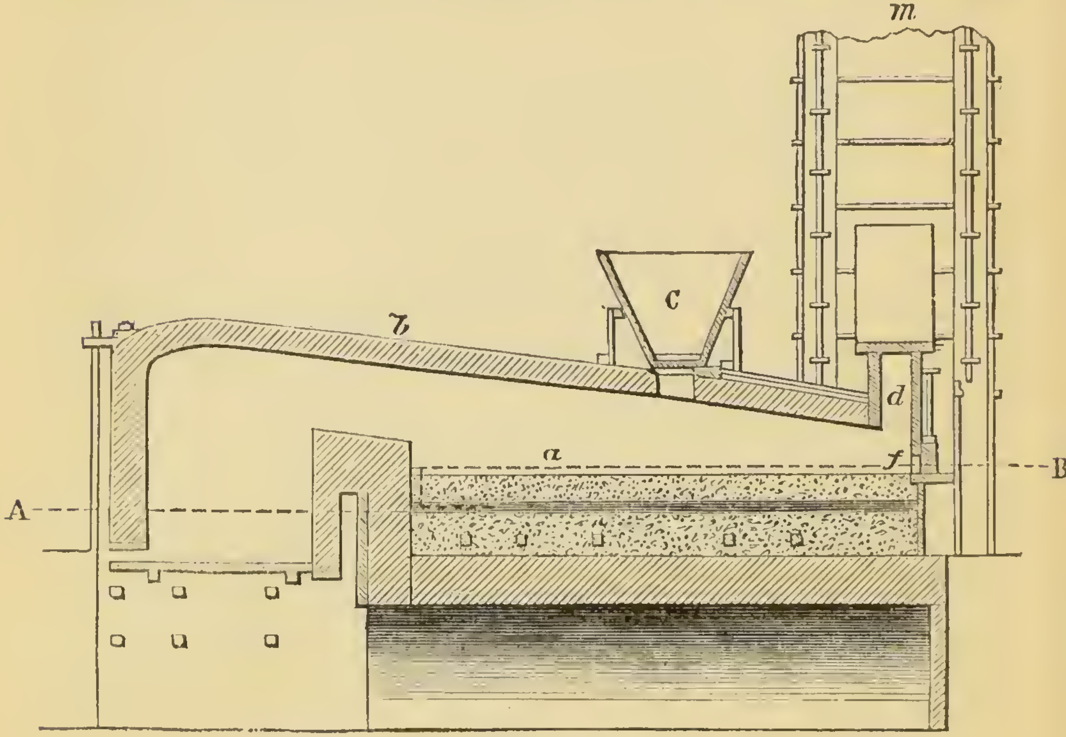


Fig. 124

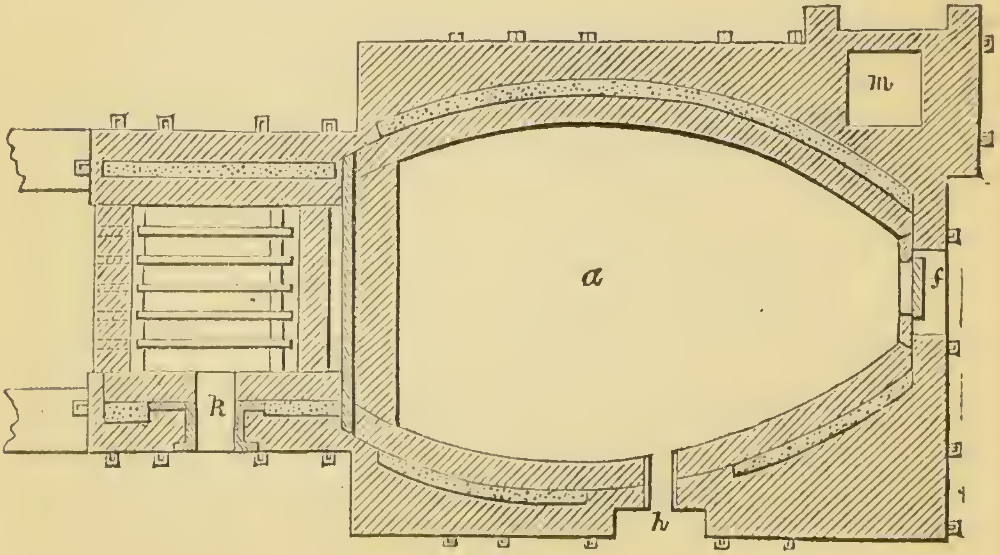


Fig. 125.

perforated bottom, standing in a cistern of water, in order to granulate it; occasionally, however, the coarse metal is cast in sand moulds, and is afterwards broken up under rollers. During this stage of the process the ferric oxide formed during the calcination is removed by the silica as a slag: its removal is facilitated by the introduction of the siliceous copper ores free from sulphur. The suboxide of copper formed during the calcination, and the copper present in the added metal-slag, react upon the ferrous sulphide still present in the roasted ore, forming copper sulphides and ferric oxide, which is also removed as a silicate. The coarse metal, crushed or granulated, is then roasted in a furnace in order to convert the remainder of the iron sulphide into oxide; and the calcined coarse metal is melted with copper ores, free from sulphur, together with the slags obtained in the final stages of previous operations. The contents of the furnace arrange themselves into two layers: the upper one consisting of metal-slag, and the lower one of *fine* or *white metal*, or copper sulphide, containing about three-fourths of its weight of copper. It is necessary to apportion the constituents of the charge with judgment, since, if the amount of copper oxide added be excessive, a certain proportion of metal separates out, together with more or less red oxide, forming a product known as *pimple copper*. If, on the other hand, the proportion of added ore be too small, more or less iron is left in the regulus, and *blue metal* is formed. The fine metal is then roasted in a reverberatory furnace, in order to convert a portion of the copper sulphide into copper oxide and sulphur dioxide; the copper oxide then reacts upon the remaining sulphide, in accordance with the equation $Cu_2S + 2CuO = 4Cu + SO_2$: metallic copper being formed and sulphur dioxide expelled. A certain quantity of slag, technically known as *roaster slag*, is also formed; it is very rich in copper and is worked up with the next charge of coarse metal. The copper is run out into sand moulds; as it solidifies considerable quantities of sulphur dioxide escape, which give to the metal a peculiar vesicular appearance; hence its name of *blister-copper*. It rarely contains above 95 per cent. of copper, the impurities mainly consisting of iron, lead, tin, arsenic, antimony, bismuth, and sulphur. To refine it the metal is heated in air in order to expel the arsenic and sulphur as oxides; afterwards it is melted and the slag which forms is skimmed off; the copper absorbs oxygen and is partially converted into oxide. A layer of anthracite dust or ground charcoal is now thrown over its surface, and the molten mass is stirred with a pole of green oak or birch. The metal in proximity to the wood appears to boil, and quantities of gas and steam are evolved. These gases, mainly hydrocarbons, produced from the wood by heat from the metal, reduce the oxides of copper, and are themselves converted into carbon dioxide and water. This operation of *poling* requires care, since, if continued too long, the copper becomes brittle; if, on the other hand, too large a proportion of suboxide be left in the metal, it also becomes brittle, and breaks with an uneven coarse-grained fracture of a purplish-red colour; and, when cast, the pigs present a peculiar longitudinal depression upon their surface. *Tough-pitch* copper, *i.e.*, properly poled copper, is soft and malleable, and possesses a lustrous silky fracture. If the copper is intended to be rolled into sheets, a small quantity of lead is added before it is cast into ingots. Occasionally the metal is poured into hot water, when it forms what is known as *bean-shot* copper; if poured into cold water, *feathered-shot* copper is obtained. In the manufacture of the purest variety of commercial copper, only those pigs are employed which are obtained towards the conclusion of the tapping. The copper obtained in the first castings contains the greater portion of the lead, nickel, arsenic, antimony, tin, etc., still remaining in the metal; it is refined by roasting and smelting, and is then known as *tile copper.* The purer pigs obtained in the first casting are refined in a similar manner, and yield a product containing but slight quantities of foreign metals, and known as *best-selected copper. Rosette copper* is obtained in thin plates of a characteristic dark-red colour by throwing water upon the surface of the molten metal, and removing the crusts of solidified metal as they are produced. *Japan copper* is cast into ingots, weighing from six ounces to a pound, which are quickly cooled after casting by throwing them into water, whereby they acquire a purple-red tint. Both varieties owe their colour to the formation of a coating of the red oxide.

In many parts of the Continent, more particularly in Sweden, Saxony, and Russia, where fuel is scarce, copper ores are smelted in blast furnaces instead of in reverberatory furnaces, as in the so-called "Welsh method" above described. The ores are first calcined in pyramidal heaps or in kilns, and a mixture of the calcined ore with coal or charcoal and *black-copper slag*, obtained at a subsequent stage of the process, is introduced into *the ore furnace*, seen in fig. 126. This furnace is about twenty feet high, and is provided with three or four horizontal twyers *a*, placed in the arch *f* of the back wall. A regulus, containing about twenty-five per cent. of copper, gradually collects in the hearth, together with a slag consisting essentially of ferrous silicate, which is run out at intervals into sand moulds, and afterwards sorted to separate any regulus which it may contain. When filled, the hearth is tapped, and the regulus is cast in sand-beds; the blocks, when cold, are broken up and roasted in kilns. The roasted mass is fused in a small blast furnace (fig. 127), with about a tenth of its weight of ore-furnace slag, the same quantity of quartz or highly siliceous copper ores, and twice the quantity of roasted *thin regulus*, obtained at the same stage in previous operations. The products of this stage are *black-copper slag*, a portion of which is afterwards worked up in the ore furnace; *thin regulus*, which contains from 60 to 70 per cent. of copper, and which, after roasting, is returned to the furnace with subsequent charges; and lastly, *black copper*, an impure metal corresponding to the blister copper of the Welsh process, the colour of which is due to a

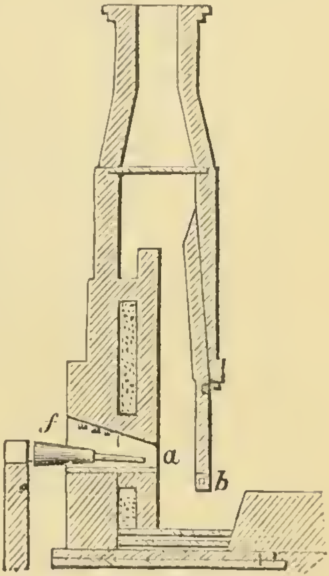


Fig. 126.

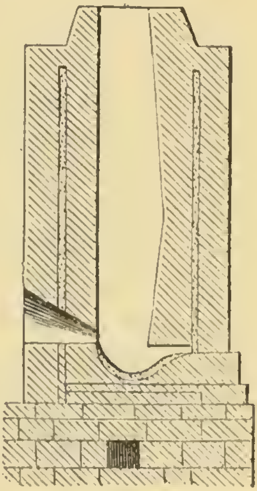


Fig. 127.

covering of the black oxide. The black copper is refined by melting it with charcoal, or coal and ground quartz, in a small blast furnace (fig. 128); a siliceous slag is gradually formed, which contains the greater portion of the metals unexpelled as oxides by the action of the blast; beneath this slag the refined metal collects. From time to time a portion is withdrawn; from its colour, lustre, and malleability the workman is able to judge of the progress of the refining operation. When sufficiently refined, the copper is ladled out into ingot moulds.

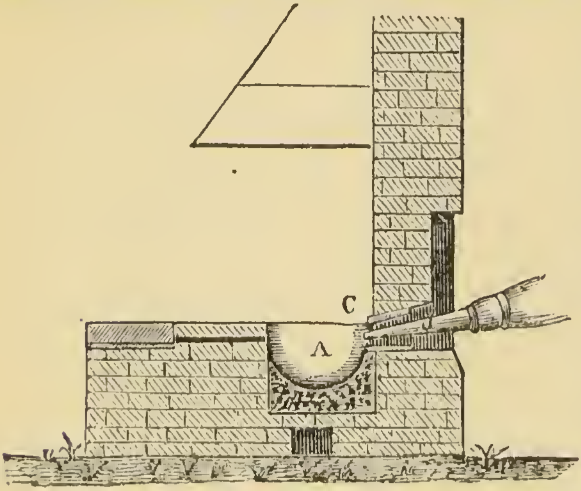


Fig. 128.

In Saxony copper-schists (*kupferschiefer*), containing only a relatively small proportion of metal, are extensively worked. Owing to their peculiar character, and to the fact of their containing a large proportion of bitumen, which materially facilitates the operation of roasting, and also a notable amount of silver which can be extracted by the Ziervogel process (see Silver, p. 136), these ores can be worked with profit even when the amount of copper is not more than three per cent. The sorted ore is roasted in kilns, whereby the water, bitumen, and a considerable portion of the sulphur, arsenic, and antimony are expelled. The roasted ore is mixed with fluor-spar and furnace residues from previous workings, and is smelted with coke in the hot-blast furnace (fig. 129). The furnace is about thirty feet high, and is provided with an arrangement for collecting the waste gases, which are used in heating the blast or in roasting the ore. The regulus or *coarse metal* is tapped at *a*, and runs into water contained in the cistern *b*, the slag is removed at *c*, and is moulded into bricks, which are used for building. The coarse metal, which contains about 30 per cent. of copper and from 0·1 to 0·3 per cent. of silver, is broken up and roasted in stalls, and is then smelted in reverberatory furnaces with sand and slag, and the *concentrated metal* or "*spurstein*," as the product is termed, is granulated by being run into water. It is next ground, roasted, and lixiviated with hot water, in order to extract the silver by the method of Ziervogel. The residue, consisting mainly of oxide of copper, is mixed with about a tenth of its weight of clay and is moulded into balls, which are dried in heated chambers, and smelted in a blast furnace with coke and a certain amount of sand, slag, and iron pyrites. The products of this stage of the process are black copper, a thin regulus rich in copper, which is smelted with a subsequent charge, and a slag, which is broken up and hand-picked in order to separate out any regulus which it may contain. The black copper is refined in the hearth already described or in reverberatory furnaces.

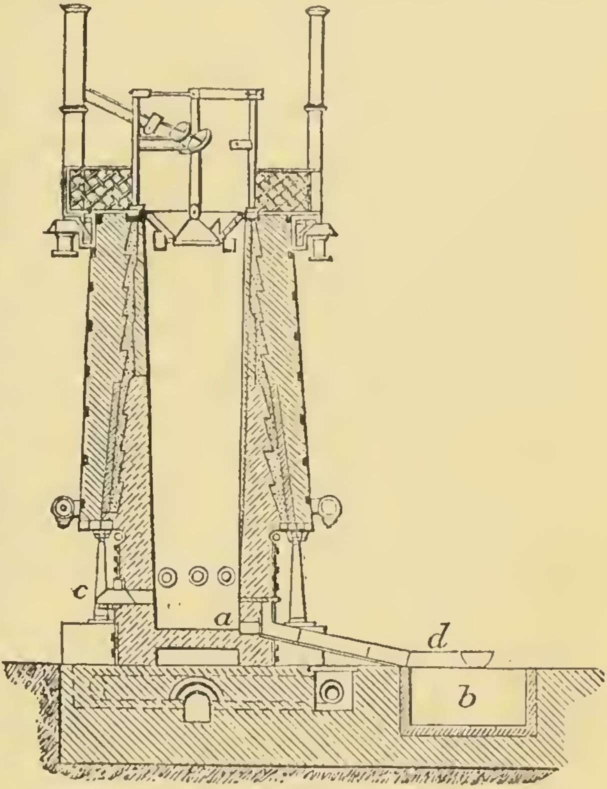


Fig. 129.

Considerable quantities of copper are now extracted from the burnt iron pyrites obtained as a bye-product in the manufacture of oil of vitriol; certain varieties of these ores, notably those from Spain, Portugal, and Norway, contain from three to five per cent. of copper. The burnt ore, which also contains about three per cent. of sulphur, is ground and calcined in a reverberatory furnace with about twelve per cent. of rock-salt, whereby the copper is converted into cupric chloride, and the sodium into sulphate. The soluble salts are extracted by lixiviation with hot water, and the copper is precipitated by the addition of scrap-iron. Certain sulphur ores contain notable quantities of silver, which is converted into chloride by roasting with common salt, the excess of salt present dissolves and aids in the solution of the silver chloride. Before treating with scrap-iron, a small quantity of potassium iodide, or zinc iodide, is added to the liquid, whereby the silver is precipitated as iodide; or the silver is thrown down, mixed with a certain quantity of copper sulphide, by the regulated action of a stream of sulphuretted hydrogen.

In the wet process of Hunt and Douglas the roasted ore, ground with water to the consistence of mud, is mixed with ferrous chloride and common salt; ferric oxide and cuprous chloride are obtained, the latter of which dissolves in the brine. On adding scrap-iron to the solution, copper is precipitated and ferrous chloride is formed, the solution of which is used in the treatment of fresh copper ores.

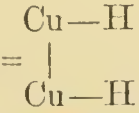
Copper has a specific gravity of about 8·92, which is but very slightly increased by hammering. It melts at about 1100°, and expands as it solidifies. It absorbs hydrogen when molten, but the gas is expelled as the metal solidifies. It is very hard, tough, and elastic, highly malleable, and ductile. It is rendered brittle by heating and slow cooling; on heating to redness and plunging it into cold water it becomes soft. It is permanent in dry air at ordinary temperatures, but in a humid atmosphere containing carbon dioxide, it gradually becomes coated with a green deposit of basic carbonate. On rubbing, it emits a faint odour; it possesses a nauseous metallic taste. Sulphuric and hydrochloric acids have little or no action upon it, even when it is finely divided, at ordinary temperatures. On heating, the sulphuric acid is decomposed in accordance with the equation,

$$Cu+2SO_4H_2=CuSO_4+SO_2+2H_2O,$$

a certain quantity of copper sulphide being simultaneously formed. Strong hydrochloric acid, on boiling with the finely-divided metal, forms cuprous chloride and free hydrogen. Concentrated nitric acid has also very little action upon it; on diluting with water, nitrogen dioxide is rapidly evolved and cupric nitrate formed,

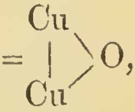
$$8HNO_3+Cu_3=3Cu2NO_3+4H_2O+2NO.$$

The exact nature of the reaction varies, however, as the solution of the metal proceeds. As the quantity of copper nitrate increases, and the acid becomes weaker, nitrogen monoxide, and, eventually, pure nitrogen are produced. Copper is gradually acted on by solution of ammonia in presence of air, and the oxide produced dissolves with the formation of a blue solution. (For alloys of copper, see Bronze, Brass, Bell-metal, etc.).

132. Copper Hydride, CuH or $Cu_2H_2 =$  $\begin{array}{l} Cu{-}H \\ | \\ Cu{-}H \end{array}$, is obtained as a reddish-brown powder by heating cupric sulphate with hypophosphorous acid. It is decomposed by heat and ignites in chlorine gas: with hydrochloric acid it gives cuprous chloride and free hydrogen,

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

133. Copper Oxides.—Copper forms two well-defined combinations with oxygen; an unstable quadrantoxide also appears to exist.

Cuprous Oxide, or **Red Oxide,** $Cu_2O =$  $\begin{array}{l} Cu \\ | \\ Cu \end{array}\!\!\Big\rangle O$, occurs native, in forms derived from the regular system, in Cornwall, in the south of France, in the island of Elba, in Siberia, and in large quantities in North America and in South Australia. It may be prepared artificially, and of a fine red colour, by adding a concentrated solution of copper sulphate to excess of caustic potash, allowing the cupric hydrate to settle, and heating it on the water-bath with a solution of sugar; or of a still brighter colour by heating one part of cupric tartrate and one of starch-sugar with two parts of potassium hydrate dissolved in sixteen parts of water. Cuprous oxide is readily reduced to the metal by heating with hydrogen, carbon monoxide, charcoal, or metallic iron. It is soluble in hydrochloric acid, forming cuprous chloride, the other mineral acids form cupric salts with separation of metallic copper. It is soluble in ammonia, forming a colourless solution, which absorbs oxygen with great rapidity and becomes blue. When melted with glass it communicates to it a fine ruby-red colour.

Cupric Oxide or **Black Oxide**, CuO, is also found native, forming the mineral known as *melaconite.* It is readily obtained by heating the metal to redness in air or oxygen, or by igniting the nitrate. It is also produced by mixing boiling solutions of caustic potash and a cupric salt. It melts at a red heat and crystallises on cooling; on heating in hydrogen or carbon monoxide, or with charcoal, potassium cyanide, or indeed with most organic bodies, it is reduced to the metallic state. Advantage is taken of this fact to determine the composition of organic substances by heating them with cupric oxide. Carbon dioxide and water are formed by the combination of the carbon and hydrogen of the organic substance with the oxygen of the oxide. Cupric oxide imparts a green colour to glass.

Cupric Hydrate, CuH_2O_2, is obtained as a greenish-blue flocculent precipitate by mixing cold solutions of caustic potash and a cupric salt. If the precipitated hydrate be heated with the liquid, containing excess of caustic potash, it becomes black, and is converted into cupric oxide. Both the hydrate and the black oxide are soluble in ammonia, forming an azure-blue solution, which has the property of dissolving cellulose, or perhaps holding it in suspension as starch is suspended in water; accordingly, the solution rapidly perforates a filter of paper or calico.

134. Copper Chlorides.—Cuprous Chloride, Cu_2Cl_2, may be formed by burning the metal in chlorine gas, or by heating it with corrosive sublimate, or by reducing cupric chloride with stannous chloride—

$$2CuCl_2+SnCl_2=Cu_2Cl_2+SnCl_4,$$

or by boiling cupric chloride with sugar, chloroform, ether, phosphorus, etc. It is a white crystalline powder, insoluble in water, but soluble in ammonia, hydrochloric acid, and solutions of many chlorides. Its ammonaical solution rapidly absorbs oxygen from the air and turns blue.

Cupric Chloride, $CuCl_2$, may be obtained by projecting copper filings into excess of chlorine gas. It forms a brown deliquescent powder which quickly becomes green by exposure to a moist atmosphere, owing to the formation of the hydrated salt $CuCl_2.2H_2O$. When perfectly dry this salt has a pale blue colour. It is more readily obtained by dissolving the oxide in strong hydrochloric acid; when concentrated the strongly-acid solution is yellow, on adding water it becomes green, and eventually, as the dilution proceeds, it changes to blue. Cupric chloride forms a large number of double salts with other metallic chlorides. The mineral *atacamite* is a hydrated cupric oxychloride of the formula $CuCl_2.3CuH_2O_2$; it is met with in Saxony, Australia, and in South America. An oxychloride of similar composition is used as a pigment under the name of "Brunswick green." Bromine forms analogous combinations with the metal.

135. **Cuprous Iodide**, Cu_2I_2, may be obtained by the direct union of its elements, or by mixing a solution of cuprous chloride in hydrochloric acid with potassium iodide; or, with the liberation of iodine, by adding potassium iodide to a solution of a cupric salt, as for example the sulphate:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

It is a greyish-white insoluble powder which fuses at a red heat. It absorbs ammonia, forming the compound $Cu_2I_2.4H_3N$.

Cupric Iodide, CuI_2, is known only in combination, as $CuI_2.4H_3N.H_2O$; this body may be obtained by exposing the above-mentioned ammoniacal compound to moist air.

136. **Sulphides.—Cuprous Sulphide**, or **Copper Glance**, Cu_2S, constitutes an important ore of the metal. It may be obtained artificially by simply triturating its constituents together in a mortar, or by suspending copper in sulphur vapour. It is a dark-grey fusible powder which may be heated to redness in steam or in chlorine without decomposition. When ignited with cupric oxide it forms metallic copper and sulphur dioxide; it is partially decomposed by heating with metallic iron with the formation of a double sulphide of copper and iron.

Cupric Sulphide, CuS, is also found native, and may be made by passing sulphuretted hydrogen into solutions of cupric salts. It is a dark-brown powder which, when moist, rapidly absorbs oxygen from the air, and is converted into copper sulphate.

A Pentasulphide of Copper, CuS_5, is said to be formed by mixing solutions of potassium pentasulphide and cupric sulphate. It is a liver-coloured powder which becomes black on drying. It is soluble in solutions of alkaline carbonates, and is not decomposed by washing with water or by exposure to air.

Combinations of copper sulphides with other metallic sulphides are frequently found native. A cuprous sulphantimonite, termed *antimonial copper* or *Wolfsbergite*, $Cu.SbS_2$, is found in the Hartz and in Spain. *Tonnenite* is a double sulphide of copper and bismuth of analogous constitution. *Copper pyrites*, or *chalcopyrite*, is a cuproso-ferric sulphide, $Cu_2S.Fe_2S_3$, and is an abundant ore of copper; it is found in tetrahedral crystals derived from the quadratic system, of a colour resembling brass; the crystals are soft enough to be cut with a knife. *Purple copper-ore* is found in crystals belonging to the regular system. A number of other varieties are known which may be regarded as mixtures of copper pyrites, and a double sulphide of iron and copper of the composition CuS.FeS.

137. Cuprous Sulphite, $Cu_2SO_3.H_2O$, is a brownish-red crystalline powder formed by treating cuprous hydrate with sulphurous acid solution. It forms double salts with the alkaline sulphites. A **cuproso-cupric sulphite**, $Cu_2SO_3.CuSO_3.2H_2O$, is obtained by mixing solutions of cupric sulphate and acid sodium sulphite.

138. Cupric Sulphate or **Blue Vitriol**, $CuSO_4$, is sometimes found native, and frequently occurs in the waters present in copper mines; by the addition of scrap-iron the metal is extracted, and comes into commerce as "cement copper." The sulphate may be obtained artificially by dissolving cupric oxide in sulphuric acid, or, on the large scale, by heating scrap or refuse copper with sulphur in a furnace so as to convert it into cuprous sulphide, which is then oxidised to cupric sulphate and oxide,

$$Cu_2S + O_5 = CuSO_4 + CuO.$$

The mass is thrown into dilute sulphuric acid, and the resulting sulphate crystallises out from the solution. It forms large blue prisms belonging to the triclinic system, of the composition $CuSO_4.5H_2O$ (figs. 130 and 131). The salt loses 4 molecules of water at 100°, and the remainder at about 200°. The anhydrous salt, which is nearly white in colour, is exceedingly hygroscopic, and is occasionally employed as a desiccating agent. It is soluble in about 3 parts of water at ordinary temperatures, and in about half its weight of boiling water; it is insoluble in absolute alcohol. Cupric sulphate dissolves in hydrochloric acid with a considerable fall of temperature, and cupric chloride is formed. The anhydrous salt is occasionally used in analysis for the absorption of vapour of hydrochloric acid. Several basic sulphates are known, some of which occur native.

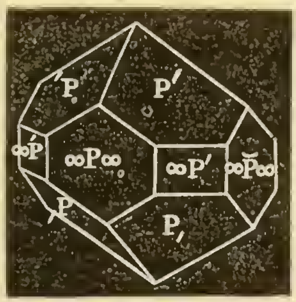


Fig. 130.

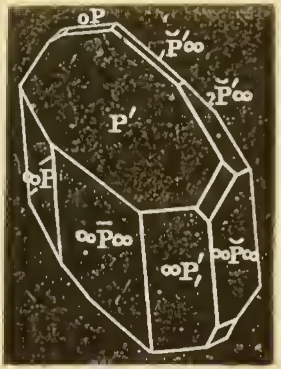
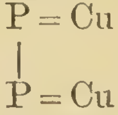


Fig. 131.

139. Copper Nitrides.—A nitride of the composition Cu_6N_2 is formed by heating cupric oxide to 250° in ammonia gas; it is a dark-green powder, which is readily decomposed, with explosion, on heating. It is violently acted upon by acids: with hydrochloric acid gas it forms sal-ammoniac and cupric chloride; chlorine gas converts it into cupric chloride and nitrogen. A chocolate-coloured nitride appears to be formed by suspending a copper ball, connected with the positive pole of a battery, in a solution of sal-ammoniac; the negative pole of the battery is connected with a platinum plate, which also dips into the solution; after a time the liquid becomes blue, and the nitride gradually collects upon the negative pole; its composition is unknown.

140. Cupric Nitrate, $Cu2NO_3$, is formed by dissolving the metal or oxide in nitric acid. It forms dark-blue prismatic crystals containing 3, 4, or 6 molecules of water of crystallization depending on the temperature of crystallization. The tri-hydrate melts at 114·5°, and boils at 170°, giving off nitric acid, and leaving a basic salt $Cu_3N_2O_8.H_2O$. A corresponding **phosphate,** $Cu_3P_2O_8$, is known. A number of basic phosphates occur native.

141. Copper Phosphides.—Copper combines readily with phosphorus, forming a grey-coloured brittle phosphide. Small quantities of phosphorus increase the fusibility and hardness of copper, and render it less susceptible to the action of sea-water. "Phosphor-bronze" is an alloy of copper and tin, containing small quantities of phosphorus.

A cupric phosphide of the composition  $\begin{array}{c}P=Cu\\ |\\ P=Cu\end{array}$ is obtained by heating cupric phosphate, $Cu_2H_2P_2O_8$, in hydrogen gas. A mixture of a body of similar composition with potassium and cuprous sulphides or levigated coke constitutes Abel's fuse, used in exploding gunpowder by magneto-electricity.

A phosphide of the composition P_2Cu_3 is formed by passing phosphoretted hydrogen over heated cuprous chloride. A phosphide of the formula Cu_6P_2, analogous to the nitride, is also known.

142. Copper Carbonates.—The normal salt $CuCO_3$ has not been definitely obtained. On adding a solution of an alkaline carbonate to a cupric salt, a greenish precipitate is formed, consisting of $CuCO_3.CuH_2O_2.H_2O$. *Malachite* has the composition $CuCO_3.CuH_2O_2$. Both carbonates, when heated to about 200°, or by long boiling with water, part with carbonic acid and water, and form cupric oxide. *Azurite*, or *blue malachite*, has the composition $2CuCO_3.CuH_2O_2$, and is found native in large crystals belonging to the monoclinic system.

143. Copper Silicates.—*Dioptase*, $CuSiO_3.H_2O$, and *chrysocolla*, $CuSiO_3.2H_2O$, are naturally-occurring monosilicates found associated with copper ores in Norway, Hungary, Cornwall, and other localities.

Compounds of copper impart a bright green colour to the non-luminous flame of the Bunsen lamp. In the oxidising zone they give to borax a green colour whilst hot, bluish green when cold: in the reducing zone the bead becomes red, especially on the addition of a trace of a tin salt, from the formation of cuprous oxide or finely-divided metallic copper. The metal is readily obtained by heating its compounds in the reducing area of the Bunsen flame with charcoal and sodium carbonate.

Very few cuprous salts can be obtained in solution. Cuprous chloride, although practically insoluble in water, dissolves to a colourless fluid in hydrochloric acid, and in solutions of certain chlorides. On exposure to air the solution becomes brown from the formation of anhydrous cupric chloride. On the addition of water white cuprous chloride is precipitated. Ammonia gradually colours the solution blue, and oxygen is absorbed. Caustic potash in excess forms a yellowish-brown precipitate of cuprous hydrate, soluble in ammonia. Potassium iodide forms insoluble white cuprous iodide without separation of iodine. Sulphuretted hydrogen and alkaline sulphides form black cuprous sulphide.

Solutions of cupric salts have usually a green or blue colour. Mixed with ammonia in slight quantity they form a green basic salt, which turns to the blue hydrate on the continued addition of the precipitant. When the ammonia is in excess, the hydrate re-dissolves, forming a deep azure-blue solution: the intensity of the colour is such that 1 part of copper in 100,000 parts of liquid may be detected by means of this reaction. The alkaline hydrates and certain of the compound ammonias precipitate hydrated blue cupric oxide when added in the cold: on boiling the precipitate with excess of the alkali it becomes black, from the formation of the anhydrous oxide. The presence of organic matter, such as sugar, tartaric and citric acids, cellulose, etc., often prevents this reaction; on the addition of potash, the solution becomes dark blue; in certain cases red or yellow cuprous oxide is formed on boiling, but the precipitation of the copper is seldom complete. The fixed alkaline carbonates form basic cupric carbonates with evolution of carbon dioxide; on heating, the precipitate is converted into the black oxide. Ammonium carbonate also forms a basic carbonate, but when added in excess it redissolves the precipitate. Potassium iodide forms cuprous iodide with separation of iodine. Sulphuretted hydrogen and alkaline sulphides form brownish black cupric sulphide, slightly soluble in excess of ammonium sulphydrate. Potassium ferrocyanide gives a characteristic brown precipitate of cupric ferrocyanide; in very dilute solutions, a dark-brown colour is produced: this reaction will detect 1 part of copper in 500,000 parts of water.

All solutions of copper, whether of cuprous or cupric salts, deposit the metal in contact with zinc or iron.

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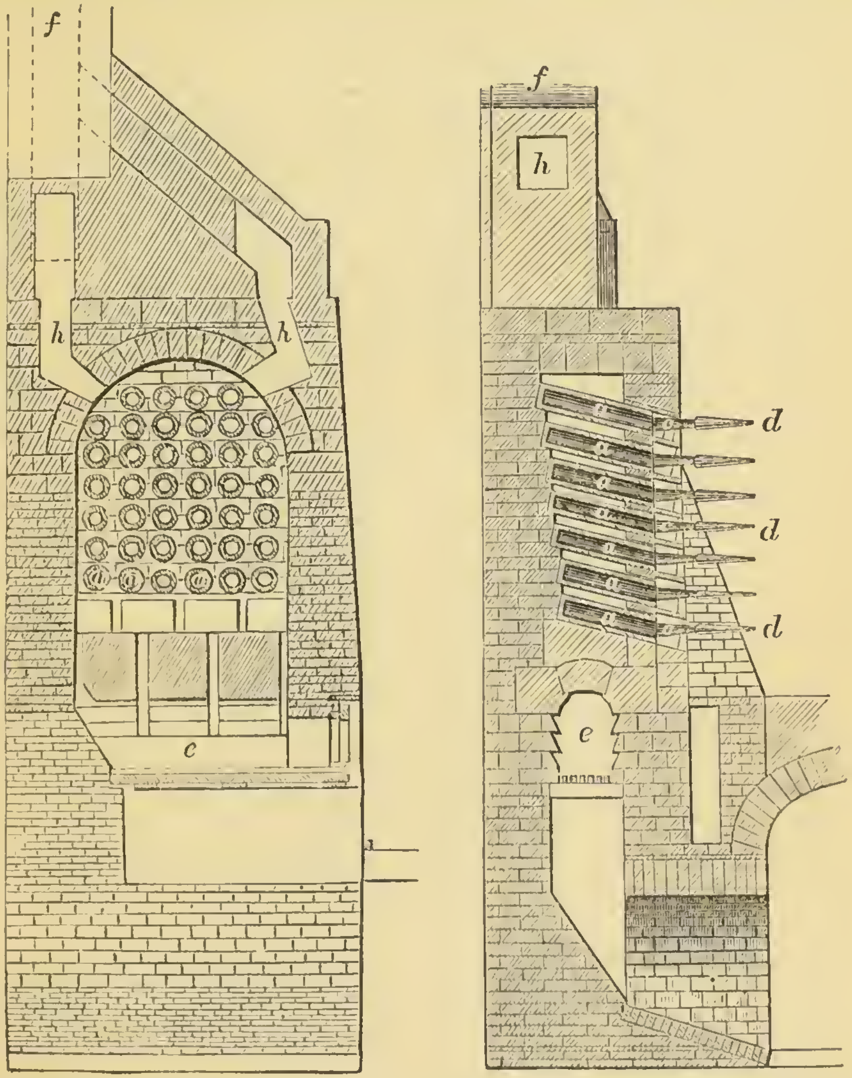
144. **Zinc**—Symbol Zn; atomic weight 65·2.—Ores of zinc were known to the ancients, and were employed by them in the manufacture of brass: it does not appear, however, that they were acquainted with the metal in an unalloyed condition. The alchemist Paracelsus, in 1541, makes mention of zinc, but it was doubtless known before his time. The principal ores of this metal are the sulphide or *blende;* the *red oxide; calamine*, or zinc carbonate; and *siliceous* or *electric calamine*, or zinc silicate. Considerable quantities of blende, or "black-jack," as it is termed by the miners, are found in Cumberland, Derbyshire, Cornwall, North Wales, and the Isle of Man. Calamine is not very abundant in this country, but a large amount is imported, principally from Spain and the United States. On the Continent zinc is chiefly smelted in Silesia, and at Vieille-Montagne, near Liége; the ore mainly employed is calamine. The red oxide is chiefly obtained from the United States: its colour is due to admixture with oxides of iron and manganese. The ores are usually dressed, picked, and afterwards roasted; the manner of conducting these operations depends upon the nature of the ore. Blende is roasted at a strong heat in a reverberatory furnace: it is thus ultimately converted into oxide, sulphur dioxide making its escape. Calamine is calcined in a furnace somewhat resembling a lime-kiln: it thus loses its carbon dioxide and water, and is converted into oxide. The roasted oxide is then mixed with ground coal, and heated in clay retorts: the reduced metal, being converted into vapour, distils over, and is collected in receivers. Three different methods of effecting this reduction are in use, known respectively as the Belgian, the Silesian, and the English process. The processes generally used are the Belgian and Silesian; indeed, most of the zinc, or *spelter* as it is termed in commerce, which is extracted in this country, is obtained by the Belgian method. The roasted ore and coal-dust, both finely-divided and intimately mixed, are placed in cylindrical clay retorts (*a*, fig. 132) supported on ledges of

masonry placed over the fireplace of a furnace, and inclined towards the front. To each retort a short clay-cone *c c* is adapted, fitted with a cone of sheet iron *d*. As soon as the bluish flame of the carbon monoxide evolved in the process of reduction changes to a greenish-white colour, due to the partial combustion of the zinc, and fumes of zinc oxide begin to be formed, the receivers are fixed to the retorts: the greater portion of the metal collects in the clay receivers, the iron cones serving to collect the zinc oxide. From time



Longitudinal Vertical Section. Fig. 132. *Transverse Vertical Section.*

to time these cones or nozzles require to be removed, and the oxide shaken out from them.

In the Silesian process the distillation is also effected from clay retorts which, however, are of a very different form from those used in the Belgian process. Fig. 133 represents a Silesian zinc furnace. The retort or muffle is seen at *a*.

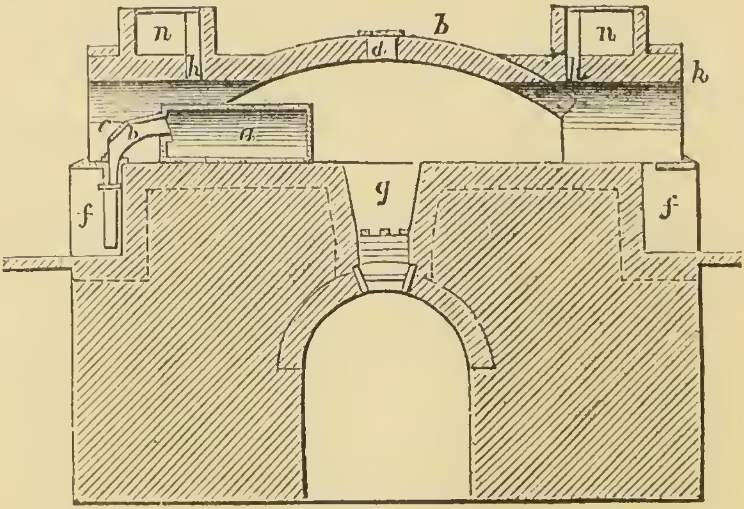


Fig. 133.

Into an aperture near the top is fitted the curved condensing tube *b*, through an opening in which (seen at *c*) the retort is charged; when the charging is finished the opening is closed by a plug. The residue, after distillation, is removed through an aperture near the bottom of the retort. About two dozen of these retorts are arranged in the furnace, in two rows, back to back. The distilled zinc escapes from the open end of the bent arm, through a cast-iron tube, and is received in the little chambers *f f*.

In the English process the reduction of the roasted ore is effected in large crucibles placed in a furnace, somewhat resembling that employed in the manufacture of glass (fig. 134). The bottoms of the Stourbridge clay crucibles *c c* are perforated, and through each orifice is placed a long sheet-iron pipe *n n*, dipping into an iron pot *pp*. The crucibles are charged from above and are not closed until the distillation commences. The distilled metal passes down the pipe, partly in powder and partly in fused masses. As the iron pipe is liable to be choked, it is necessary to clear it from time to time by inserting an iron rod into it. The rough zinc obtained by each of the methods is re-melted in iron, or better, in clay pots, freed from oxide by stirring and skimming, and cast into cakes or ingots.

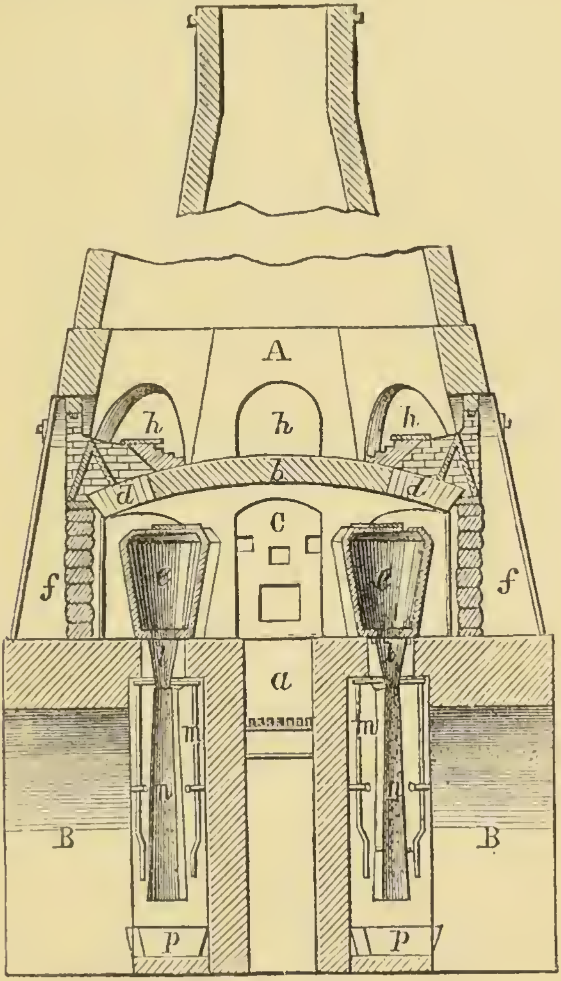


Fig. 134.

Commercial zinc usually contains more or less iron, lead, tin, cadmium, copper, and arsenic. To obtain it chemically pure the metal is dissolved in a slight excess of sulphuric acid, the solution is treated with sulphuretted hydrogen, filtered, and mixed with a solution of sodium carbonate; the precipitated zinc carbonate is washed, converted into oxide by ignition, and mixed with charcoal obtained from sugar, and redistilled from a porcelain retort.

Zinc is a hard, brittle, bluish-white metal; when fractured it exhibits a highly crystalline structure. When pure, it may be rolled out into thin leaves at the ordinary temperature, but when mixed with other metals it is malleable only at about 120°; at a still higher temperature it again becomes brittle, and may readily be reduced to powder. The density of zinc varies from about 6·86 to 7·2. It melts at 423°, and boils at 1040°. Zinc experiences very little alteration in air, but in contact with water charged with carbonic acid, it is partially converted into an oxycarbonate. When strongly heated in air or in oxygen, it burns with a greenish-white flame, producing dense white fumes of the oxide. Zinc is now largely used for *galvanising* iron; the iron is coated with a thin layer of zinc by immersion in a bath of melted metal; it is thus protected from oxidation. Pure zinc dissolves slowly in the ordinary mineral acids, but the commercial variety, containing foreign metals, is rapidly attacked with production of hydrogen. The same rapid action in the case of the pure metal may be induced by placing it in contact with platinum or copper. Zinc and copper in intimate connection decompose water even at the ordinary temperature; at a gentle heat, the decomposition is very rapid (Vol. I., p. 53). Caustic alkalies also dissolve zinc with formation of an oxide and free hydrogen. Zinc readily unites with the greater number of the metals, forming hard and often brittle alloys.

Brass is an alloy of 1 part of zinc and 2 parts of copper, prepared by adding zinc to molten copper contained in fireclay crucibles. Frequently old brass is added to the mixture; the old brass being first placed in the crucible, which is then filled up with alternate layers of zinc, copper, and powdered coal or charcoal, the latter body being added to reduce any oxide formed during the melting. When the charge is melted the surface is skimmed, and the alloy cast in iron or sand moulds. *Muntz's metal*, which is used extensively as a sheathing for ships, is an alloy of 3 parts of copper and 2 parts of zinc, with a small quantity of lead, and occasionally of tin. It is made by melting the copper on the hearth of a reverberatory furnace, and mixing with it the requisite quantity of zinc. This alloy, unlike ordinary brass, can be rolled at a red heat, and is stated to be less easily fouled than the ordinary copper ship-sheathing. *Pinchbeck* is an alloy of 3 parts of copper to 1 of zinc; *Dutch* and *Mannheim gold* have a similar composition; *Tombac* contains about 4 parts of copper and 1 of zinc. Lead is occasionally added to brass in order to facilitate its working in the lathe. *Aich's metal* and *sterro-metal* are varieties of brass containing iron and tin.

145. **Zinc Oxide**, ZnO, the only known compound of oxygen and zinc, occurs native as *red zinc ore*, and, combined with ferric and manganic oxides, as *franklinite*. It may be formed artificially by the ignition of the metal in air or in oxygen, or by heating certain zinc salts, such as the carbonate and oxalate. The oxide prepared by burning the metal is employed as a pigment under the name of *zinc white;* it is chiefly valued from its permanency, as it is not blackened by exposure to sulphuretted hydrogen like white lead. As thus procured it is an amorphous powder of specific gravity 5·6; by heating zinc chloride in a current of steam the oxide may be obtained in six-sided prisms of a density 6·0. Both forms of the oxide on heating acquire a transient yellow colour.

146. **Zinc Hydrate**, ZnH_2O_2, is obtained as a white gelatinous precipitate by adding ammonia to a solution of a zinc salt. The same hydrate may be obtained crystallised by placing zinc in contact with iron, lead, or copper in dilute ammonia water. A **dihydrate**, ZnH_4O_3, or $ZnH_2O_2.H_2O$, is obtained in transparent octahedrons by allowing a saturated solution of the oxide in sodium hydrate to remain exposed to the air. Both these hydrates readily part with their water on heating; they are easily dissolved by dilute acids, by potash and soda, and by ammonium carbonate.

147. **Zinc Chloride**, $ZnCl_2$, may be formed by the direct union of its elements, or as a crystallised hydrate, $ZnCl_2.H_2O$, by dissolving the metal in hydrochloric acid, and evaporating the solution. The anhydrous chloride is a greyish-white, highly caustic, waxy-looking substance; it is readily fusible, and may be distilled. It deliquesces rapidly on exposure to moist air, and is very soluble in water and in alcohol. The anhydrous chloride acts as a powerful dehydrant: it chars wood, converts alcohol into ether, camphor into cymene, morphine into tetrapodimorphine (apomorphine),

etc.; a concentrated solution cannot be filtered through paper, as it attacks and dissolves vegetable fibre. Zinc chloride in dilute aqueous solution is used as an antiseptic, under the name of "Burnett's disinfecting fluid." A strong solution of the chloride dissolves zinc oxide, forming an oxychloride, $ZnCl_2.3ZnO.4H_2O$, crystallising in octahedrons. Its solution dissolves silk, and may be used for separating this fibre from wool. Zinc oxychlorides are also used as pigments, as cements, and for making artificial teeth.

148. **Zinc Bromide**, $ZnBr_2$, and **Zinc Iodide**, ZnI_2, are deliquescent crystalline substances obtained by the direct union of their elements. They unite with ammonia, and with alkaline bromides and iodides, forming double salts.

149. **Zinc Sulphide**, ZnS, occurs as *blende*, and constitutes an important ore of the metal. Pure zinc sulphide is white, but it is generally found more or less dark-coloured from the presence of iron; occasionally it is met with possessing a yellow, red, or green colour. Blende occurs associated with galena and silver ores, with copper-pyrites and heavy spar in the Hartz, in Hungary, in Cornwall, Derbyshire, and Cumberland. Its specific gravity is about 3·92, and it is almost infusible. Hydrated zinc sulphide, $ZnS.H_2O$, is easily obtained by passing sulphuretted hydrogen through a neutral solution of a zinc salt, or by the addition of ammonium sulphide. It is readily soluble in dilute mineral acids, but is nearly insoluble in acetic acid.

☞ A **pentasulphide**, ZnS_5, is said to be formed by adding a solution of potassium pentasulphide to a neutral solution of a zinc salt. It is a white powder when moist, but acquires a bright yellow colour on drying.* Several zinc oxysulphides are known.

150. **Zinc Sulphate**, or **White Vitriol**, $ZnSO_4$, is formed as a bye-product in the preparation of hydrogen by the action of sulphuric acid on zinc. On the large scale it is obtained by roasting blende, and lixiviating the roasted mass with water. It crystallises with 7 molecules of water, and is

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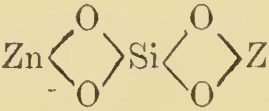
[*] Attempts made in the author's laboratory to obtain this compound gave a negative result. Follenius has shown that the so-called cadmium pentasulphide is a mixture of the monosulphide and sulphur.

isomorphous with magnesium sulphate. It parts with 6 molecules of water at 100°, but retains the last molecule up to 250°. The salt is soluble in less than its own weight of water at ordinary temperatures. Zinc sulphate is used in calico-printing and in medicine. It combines with the alkaline sulphates and with magnesium sulphate to form double salts.

151. Zinc Carbonate, $ZnCO_3$, is found native as *calamine*, and constitutes the most abundant ore of the metal. The normal salt cannot be formed artificially in the wet way; by adding a solution of an alkaline carbonate to a zinc salt in solution various oxycarbonates are formed, the composition of which depends upon the temperature and degree of concentration of the fluids.



152. Zinc Orthosilicate, Zn_2SiO_4, or $\mathrm{Zn}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{Si}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{Zn}$, occurs native as *willemite*. *Siliceous calamine*, used to some extent as an ore of zinc, is a hydrated orthosilicate, $Zn_2SiO_4.H_2O$. It is found in unsymmetrically-terminated rhombic prisms (see fig. 135). Like tourmalin, boracite, sugar, and other unsymmetrical crystals, it is *pyro-electric*, that is, on warming, one end becomes positively, the other negatively electrified.

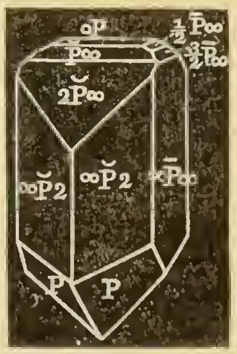


Fig. 135.

Compounds of zinc heated in the Bunsen flame with cobalt nitrate acquire a bright green colour. When neutral, or when mixed with sodium acetate, their solutions give a white precipitate of the sulphide with sulphuretted hydrogen. Ammonium sulphide forms the same compound. The fixed alkaline carbonates give a white basic carbonate, with evolution of carbon dioxide; this precipitate is soluble in alkalies, and in ammonium chloride. Potash, ammonia, and ammonium carbonate give precipitates soluble in excess of the precipitant, but they are reprecipitated on dilution with boiling water.

153. **Cadmium**—Symbol Cd; atomic weight 112.—Compounds of this metal occur associated with zinc ores; as cadmium is more volatile than zinc it is mainly found in the first portion of the distilled metal when the ores are reduced by carbon. Cadmium was discovered by Stromeyer in 1818; its name is derived from *cadmia fossilis.* It is a silver-white crystalline metal of specific gravity 8·6; it melts at 320°, and boils at 860°. It is readily dissolved by mineral acids, under ordinary conditions: contact with platinum preserves it from the action of strong nitric acid. It forms a number of alloys with other metals.

Cadmium unites with oxygen in two proportions to form a suboxide, Cd_2O, and a monoxide, CdO.

The **suboxide,** $\begin{matrix}Cd\\Cd\end{matrix}\!\!>O$, is a green powder obtained by heating cadmium oxalate.

The **protoxide** may be formed by burning the metal in air or in oxygen, or by igniting the carbonate or nitrate. It is a dark-brown infusible powder of specific gravity 6·65. It is obtained hydrated, and of a white colour, by the addition of potash to a solution of a cadmium salt. The precipitate absorbs carbonic acid, is readily soluble in dilute acids and in ammonia, but is insoluble in ammonium carbonate.

154 **Cadmium Chloride,** $CdCl_2$, is a white crystalline, fusible, volatile salt. It usually occurs with one atom of water of crystallization. It readily unites with other chlorides to form well-crystallised double salts.

155. **Cadmium Bromide and Iodide** are very similar in appearance and properties to the chloride: they are employed in photography.

156. **Cadmium Sulphide,** CdS, is obtained as an orange-yellow powder by passing sulphuretted hydrogen through solutions of cadmium salts. On heating it darkens in colour, and at a high temperature becomes bright red. It is readily soluble in ammonia and nitric acid, but dissolves very sparingly in dilute hydrochloric acid, more easily in the concentrated acid. It is insoluble in ammonium sulphide. The very rare mineral *Greenockite* consists of cadmium sulphide.

157. **Cadmium Sulphate,** $CdSO_4$, is formed by dissolving the oxide in sulphuric acid. When deposited from solutions

at ordinary temperatures the crystals have the composition $3CdSO_4.8H_2O$; but when crystallised from the heated liquid the salt contains only 1 molecule of water.

Solutions of cadmium salts afford the yellow sulphide on the addition of sulphuretted hydrogen: it is distinguished from arsenic sulphide by its insolubility in ammonium sulphide. Ammonia forms the hydrate, readily soluble in excess.

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158. **Palladium**—Symbol Pd.; atomic weight 106·6.—This metal was discovered by Wollaston in 1803. It occurs associated with platinum and gold in several districts in South America, and is extracted by treating the ore with nitrohydrochloric acid, precipitating the platinum by means of ammonium chloride, and adding mercuric cyanide to the filtered solution: on heating the palladium cyanide thus formed, the metal is obtained as a grey spongy mass.

Palladium, when compact, has a white colour, and possesses a lustre almost equal to that of silver. Its specific gravity is about 12·0; it is malleable and ductile, and may be fused at a white heat. In the oxyhydrogen flame it is volatilised, forming a green vapour. It is less permanent in the air than platinum; when heated it experiences superficial oxidation; when melted it absorbs oxygen, but, as in the case of silver, the greater portion of the gas is evolved when the metal solidifies. When used as the negative electrode in the electrolytic decomposition of water, palladium may be made to absorb about 0·5 per cent. of its weight of hydrogen: the gas may be expelled at a red heat *in vacuo*, leaving the metal as a spongy porous mass.

Palladium is dissolved by nitric acid: it is scarcely attacked, however, by hydrochloric or sulphuric acid; hydriodic acid and free iodine coat it with the black palladium iodide. Palladium has been used for the graduated scales of physical instruments, and in the manufacture of weights of precision. An amalgam of palladium is occasionally employed by dentists for the purpose of filling teeth.

159. **Palladium Monoxide**, PdO, is a dark-grey powder obtained by heating the nitrate to low redness; at a bright

red heat it is resolved into the metal and oxygen. The corresponding hydrate is a brown powder formed by adding sodium carbonate to a solution of palladium dichloride.

The **dioxide**, PdO_2, is not known in the free state. On adding potash or its carbonate to a solution of palladium tetrachloride, a brown hydrated palladic oxide is formed containing alkali. The precipitate is soluble in strong hydrochloric acid, apparently without decomposition; with the dilute acid it readily yields chlorine gas.

160. Palladium Dichloride, $PdCl_2$, is a dark-brown powder formed by dissolving the metal in strong hydrochloric acid containing a small quantity of nitric acid, and evaporating the solution to dryness. It forms double salts with alkaline chlorides analogous to the corresponding platinum compounds.

The **tetrachloride**, $PdCl_4$, is obtained by dissolving the metal or the dichloride in aqua-regia. When concentrated its solution is intensely brown: when heated it readily parts with chlorine. The **chloro-palladinates**, M_2PdCl_6, possess a deep crimson colour; and are easily decomposed on heating: they are strictly analogous to the corresponding platinum compounds with which they are isometric.

161. Palladium Di-iodide, PdI_2, is a black powder formed by adding potassium iodide to a solution of palladium dichloride. It is almost completely insoluble in water: iodine is occasionally determined in quantitative analysis as the di-iodide.

162. Ammoniacal Palladium Compounds.—On adding ammonia in slight excess to a solution of palladium dichloride a red precipitate of the composition $(NH_3)_2.PdCl_2$ is obtained. When heated, or when dissolved in excess of ammonia and re-precipitated by addition of an acid, the colour of the substance changes to yellow. This yellow modification is soluble in an aqueous solution of potash without loss of ammonia. It is the **palladamine chloride**; the base may be obtained free by digesting the compound with silver oxide and water; its composition is N_2H_6PdO. It is readily soluble in water; its solution has a strong alkaline reaction, and absorbs carbon dioxide. It forms salts with acids, which crystallise easily. A compound having the composition $4NH_3.PdCl_2$ crystallises from the ammoniacal solution of the preceding body. It also undergoes a molecular change into a compound which may be termed **pallad-diamine chloride.** The base, $N_4H_{12}Pd_2O_2$, may be obtained from the chloride in the same way in which the oxide of palladamine is formed from its salts. It is a crystalline body soluble in water: its solution is strongly alkaline, and liberates ammonia from ammonium chloride: it dissolves oxide of silver, but precipitates solutions of copper, nickel, iron, cobalt, and aluminium.

Palladium compounds yield the black sulphide on addition of sulphuretted hydrogen: the precipitate is insoluble in ammonium sulphydrate. Potassium iodide yields the black iodide; mercuric cyanide the white cyanide, $PdCy_2$. Stannous chloride gives a black precipitate soluble in hydrochloric acid with the formation of an intensely green liquid.

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163. Mercury—Symbol Hg (Hydrargyrus); atomic weight 200.—This element has been known from very remote times, and certain of its compounds were used by the Greeks and Arabians. By the alchemists it was known under the sign of the planet Mercury, ☿ The metal is found free and in union with gold and silver, but its chief source is the sulphide or *cinnabar*, which occurs in quantity at Almaden in Spain, and at Idria in Illyria. It is also met with in China, Peru, Mexico, California and Borneo.

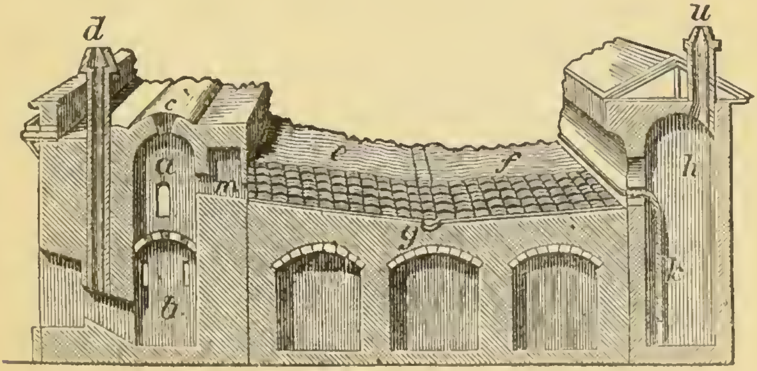

Fig. 136.

At Almaden, the ore is simply roasted in the chambers *a* in fig. 136, and the mixed vapours of mercury and sulphur dioxide pass through a series of pear-shaped vessels made of earthenware, *ef*, termed *aludels*, in which the greater portion of the metal condenses, and flows into the trough *g*. Fig. 137 shows the manner in which the aludels are connected together.

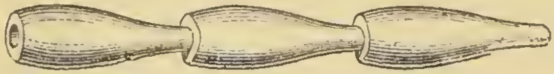
Fig. 137.

In the Idrian works the fumes from the roasted ore are led into a number of chambers, covered with iron plates and cooled by water, in which the mercury condenses. Figs. 138, 139, and 140 show the arrangement of the Alberti furnace which is now used with great economy in the treatment of Idrian ores, more especially of the poorer varieties. The ore is placed on the hearth of the reverberatory furnace *a*, and the gases and mercurial vapours produced by roasting pass into the brick condensing chamber *c*, and thence through a wide cast-iron pipe *d*, cooled by water, into a second condensing chamber *ee* divided into two storeys; from the upper storey *f* the gaseous products pass through a second iron tube *g*, also cooled by water, and opening into a chamber *h*: from this chamber the vapours find their way into the stack by a series of flues in which nearly the whole of the remaining traces of the mercury are deposited, partly as metal, partly as oxide and sulphide. The condensation in the Alberti furnace is nearly perfect, upwards of 90 per cent. of the mercury being deposited in the lower iron tube. Unlike the older processes, this method can be worked continuously for lengthened periods, that is, until the draught in the flues is interrupted by the condensed solid product.

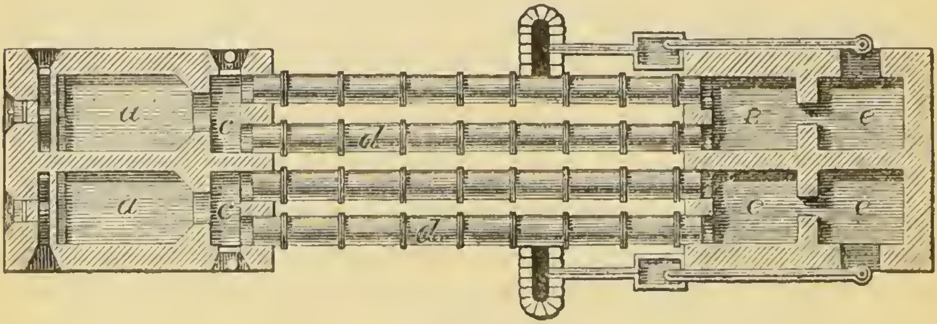

Fig. 138.

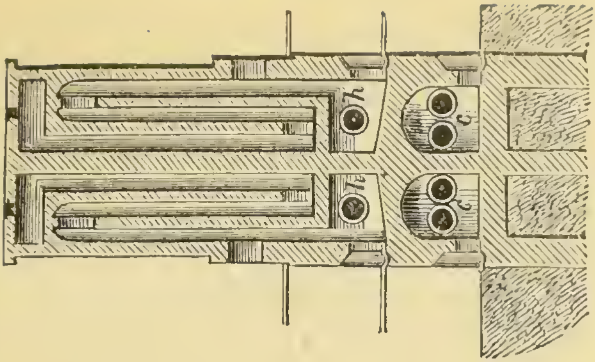

Fig. 140.

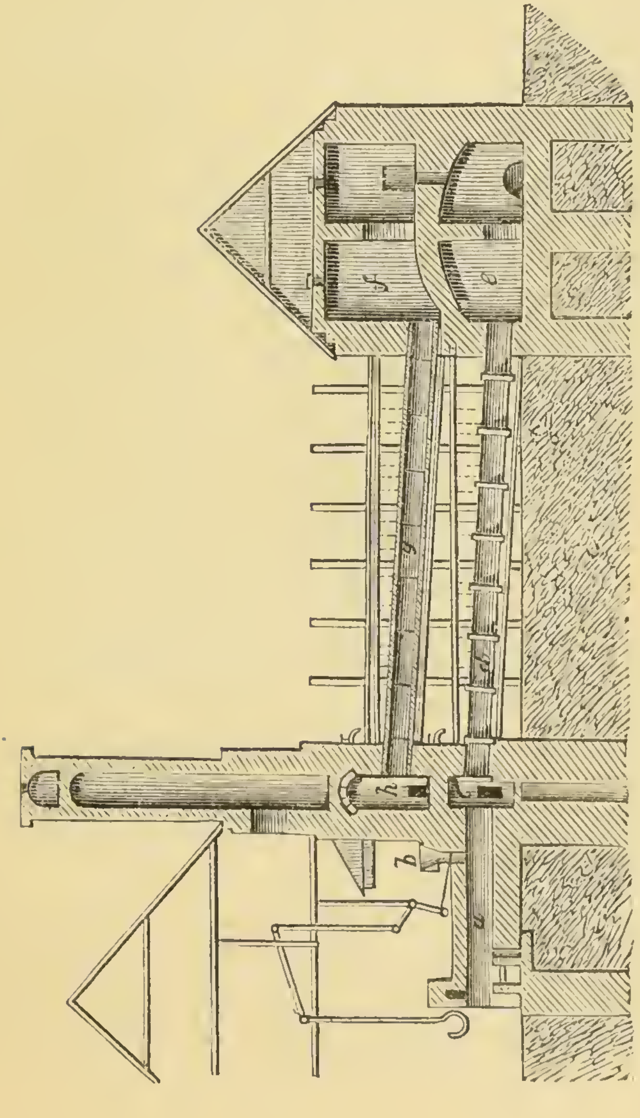

Fig. 139.

At Landsberg in Bavaria, and in California, the coarsely-powdered ore is mixed with quick-lime and heated in long cast-iron retorts *a*, arranged as in gas-works (fig. 141). The charge is introduced at the back of the retort, the gaseous products passing through the pipe *c* into water contained in the main *d*, which is cooled by a flow of cold water round it. The reaction may be thus expressed—

$$4HgS + 4CaO = 3CaS + CaSO_4 + 4Hg.$$

As found in commerce mercury usually contains more or less lead, zinc, and bismuth, from which it may be freed by digesting it with dilute nitric acid. Mercury has a specific gravity of 13·596 at 0°, compared with water at 4°: it is the heaviest liquid known. It freezes at − 40° forming a ductile malleable mass, and boils at 357° forming a colourless vapour: it volatilises, however, even at ordinary temperatures. When pure it is permanent in the air or in oxygen: if mixed with foreign metals it becomes coated with a greyish powder on being agitated in air; mercury thus contaminated is found to leave a *tail* or streak when running along a smooth surface. When heated to a high temperature in air it gradually absorbs oxygen and becomes coated with a film of the red oxide. Hydrochloric acid has scarcely any action on mercury; concentrated sulphuric acid attacks it when heated, with formation of mercuric sulphate and evolution of sulphur dioxide. Nitric acid readily dissolves it, producing, with excess of mercury, mercurous nitrate; with excess of acid, mercuric nitrate.

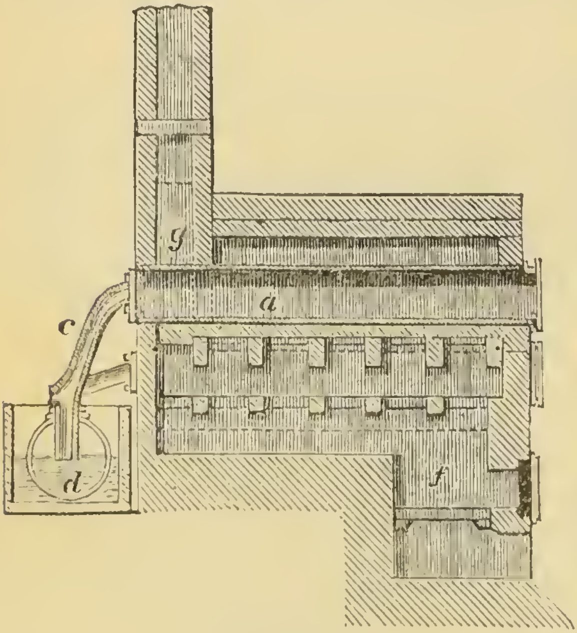

Fig. 141.

Mercury readily alloys, or *amalgamates* with other metals, forming, in many cases, definite chemical combinations: several of these amalgams are employed in the arts. Sodium amalgam is used in the extraction of metals; tin amalgam in the manufacture of mirrors, amalgams of tin, gold, and silver are employed by dentists. Sodium amalgam, which is readily decomposed by contact with water, with liberation of hydrogen, is frequently employed in chemical research as a reducing agent; and an amalgam of tin and zinc is used for the rubbers of electrical machines. Silver amalgams of variable composition are found native in forms derived from the regular system.

164. Two oxides of mercury are known, viz., *mercurous* and *mercuric oxides.*

Mercurous Oxide, Hg_2O, is a dark-brown powder formed by the action of caustic potash on calomel. It is readily resolved on exposure to light, or by simple trituration in a mortar, into mercury and mercuric oxide.

Mercuric Oxide, HgO, has long been known, and was frequently prepared by the alchemists. It may be obtained by heating the metal in air or by calcining the nitrate: as thus made it is a bright-red crystalline powder. It may also be formed of an orange-yellow colour by the addition of caustic potash to a solution of corrosive sublimate. It darkens on heating, becoming almost black, but recovers its original colour when cold. It is slightly soluble in water; and the solution has an intense metallic taste. At a low red heat it is completely resolved into oxygen and mercury. It explodes when heated with sulphur and the alkaline metals: many finely-divided metals, such as zinc and tin, are readily oxidised when heated with the oxide. It is quickly acted upon by chlorine, forming, at a low temperature, chlorine monoxide and an oxychloride of the metal: when heated, oxygen and mercuric chloride are alone produced.

165. Mercury forms two combinations with chlorine, corresponding to the oxides: several oxychlorides are also known.

Mercurous Chloride or **Calomel**, Hg_2Cl_2, is frequently found native, associated with the sulphide, and may be obtained by heating the metal with chlorine, or the mercuric chloride with mercury, or with reducing agents such as sulphurous oxide. It is also made by heating a mixture of mercurous sulphate and common salt:

$$Hg_2SO_4 + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

The mixture is heated in iron cylinders or retorts, and the calomel which vapourises is condensed in a small brick chamber as a loose powder, which must be washed with water to free it from accompanying mercuric chloride.

Calomel is a white powder which becomes slightly yellow on heating. At a low red heat it volatilises without previous fusion. It is almost insoluble in water. It is quickly reduced to the state of metal on boiling with stannous chloride: when digested with potassium iodide it yields mercurous iodide and potassium chloride. It is dissolved by nitric acid with formation of corrosive sublimate and mercuric nitrate and evolution of nitrogen dioxide:

$$3Hg_2Cl_2 + 8HNO_3 = 3HgCl_2 + 3Hg(NO_3)_2 + 2NO + 4H_2O.$$

Calomel is completely decomposed when heated with potash or soda, thus:

$$Hg_2Cl_2 + 2KHO = Hg_2 + O + 2KCl + H_2O.$$

By treatment with ammonia gas or solution of ammonia, calomel is turned black, owing to the formation of *mercuroso-ammonium chloride*, NH_3HgCl. By long continued boiling with water, calomel is decomposed into a grey compound of the metal and mercurous chloride, and into corrosive sublimate which dissolves: dilute hydrochloric acid or solutions of alkaline chlorides heated with calomel ultimately convert it into mercuric chloride.

Mercuric Chloride or **Corrosive Sublimate**, $HgCl_2$, is produced by the action of chlorine on the metal, or on the preceding compound. It is commonly made by heating a mixture of mercuric sulphate and sodium chloride; mercuric chloride sublimes and sodium sulphate remains; or by adding hydrochloric acid to a hot and concentrated solution of mercurous nitrate:

$$Hg_2(NO_3)_2 + 4HCl = 2HgCl_2 + 2H_2O + 2NO_2.$$

Mercuric chloride crystallises in forms belonging to the rhombic system. It fuses at 302°; is sparingly soluble in cold water, more soluble in hot water; 100 parts of water at 10° dissolve 6·5 parts of the salt: 100 parts at 100° dissolve about 59 parts. It is very soluble in alcohol and ether: when an aqueous solution of mercuric chloride is agitated with ether the greater portion of the salt is found in the ethereal layer. Hydrochloric acid dissolves the salt, forming a compound of the composition $(HgCl_2)_2.HCl$. Mercuric chloride combines with many chlorides to form readily crystallisable salts: the preparation known as *sal alembroth* has the formula $2NH_4Cl.HgCl_2.H_2O$.

Ammonia gas is absorbed by the salt, forming a product of the composition $HgCl_2.NH_3$, which may be distilled at a high temperature without decomposition.

By the addition of potash to a solution of mercuric chloride in quantity insufficient to precipitate the whole of the mercury as mercuric oxide, or by digesting mercuric chloride solution with mercuric oxide, various oxychlorides of mercury are obtained, containing 2, 3, or 4 molecules of the oxide to 1 molecule of the chloride. They are yellow, red, or brown crystalline powders, which yield mercuric oxide on treatment with potash.

166. **Mercurous Bromide,** Hg_2Br_2, is a yellowish-white powder, insoluble in water, and vapourisable at a low red heat. **Mercuric Bromide,** $HgBr_2$, is formed by the direct addition of mercury to bromine, or by agitating bromine water with the metal. It is sparingly soluble in cold water, readily soluble in hot water, and forms crystals isomorphous with those of the chloride. It forms oxybromides similar to the corresponding oxychlorides.

167. **Mercurous Iodide,** Hg_2I_2, may be obtained by triturating its constituents in atomic proportions, mixed with a little alcohol, or by heating the materials together in a closed flask at a temperature not exceeding 250°. It is thus obtained in well-defined rhombic crystals of a fine dark-red colour when hot, but which change to yellow on cooling. It may also be formed by adding potassium iodide to mercurous nitrate. As ordinarily obtained it is a yellowish green powder, which, when moist, is blackened by exposure to light. By adding iodine to the solution of the potassium iodide before mixing with the mercurous nitrate, **mercuroso-mercuric iodide,** Hg_4I_6 or $Hg_2I_2.2HgI_2$, is formed: it is intermediate in composition between the mercurous and mercuric

iodides. It is a yellow insoluble powder which darkens on heating, and may be sublimed without decomposition.

Mercuric Iodide, HgI_2, may be formed by the direct addition of iodine to mercury, or, better, by mixing solutions of mercuric chloride and potassium iodide. At the moment of formation the precipitate is yellow, but quickly becomes red: if the change be observed under the microscope it is seen that the yellow rhombic plates first produced are transformed into scarlet octahedrons derived from the quadratic system. When the scarlet iodide is heated it turns yellow, melts, and sublimes in beautiful yellow rhombic prisms. The salt gradually recovers its original red colour on standing: on touching the crystals with a solid body they are instantly converted into the red modification. Mercuric iodide forms double salts with many metallic chlorides and iodides.

168. **Mercurous Fluoride**, Hg_2F_2, and **Mercuric Fluoride**, HgF_2, are unstable combinations formed by dissolving the corresponding oxides in hydrofluoric acid.

169. **Mercurous Sulphide**, Hg_2S, is a black powder obtained by the action of sulphuretted hydrogen on mercurous salts, best on the acetate. It is decomposed on heating into mercuric sulphide and free mercury.

Mercuric Sulphide, HgS, is found native in forms derived from the hexagonal system: it constitutes the principal ore of mercury, and has long been used as a pigment under the name of *vermillion* or *cinnabar*. As prepared by triturating mercury and sulphur it is black, and is known in pharmacy as *Æthiops mineralis.* It is also obtained of a black colour by passing excess of sulphuretted hydrogen through a solution of corrosive sublimate. It is but slightly acted upon by nitric acid, but dissolves in aqua-regia: it is also soluble in solution of potassium sulphide, with which it forms a crystalline compound of the formula $K_2HgS_2.5H_2O$.

Cinnabar is made artificially on the large scale as a pigment by triturating mercury and sulphur together and heating the black sulphide until it sublimes. The best vermillion comes from China: the brightness of the colour varies with the mode of preparation and with the degree of subdivision of the product.

170. **Mercurous Sulphate**, Hg_2SO_4, is a white, sparingly

soluble, crystalline powder, formed by adding sodium sulphate to mercurous nitrate.

Mercuric Sulphate, $HgSO_4$, is formed by heating mercury with excess of sulphuric acid. It melts at a high temperature, and may be volatilised unchanged. It is decomposed by hydrochloric, hydriodic, and hydrocyanic acid gases. On digestion with water it is decomposed into an insoluble basic salt known as *turbith* or *turpeth mineral* or trimercuric sulphate, $HgSO_4.2HgO$; and into an acid salt, $HgSO_4.2SO_3$. On passing a small quantity of sulphuretted hydrogen into the solution, a white flocculent precipitate is formed of the composition $2HgSO_4.HgS$.

171. Mercurous Nitrate, $Hg_2(NO_3)_2.2H_2O$, is a white crystalline salt, obtained by dissolving the metal in cold dilute nitric acid. If excess of the metal be present a basic nitrate, $Hg_2(NO_3)_2.2Hg_2O.3H_2O$, is formed, which is decomposed on treatment with water. Several other basic nitrates are known. On adding ammonia to a solution of mercurous nitrate a black precipitate of variable composition, known in pharmacy as *mercurius solubilis Hahnemanni*, is formed.

Mercuric Nitrates.—A highly concentrated solution of mercuric oxide in strong nitric acid forms a thick syrupy liquid which refuses to crystallise. On adding strong nitric acid to the solution a crystalline precipitate is formed of the formula $2Hg(NO_3)_2.H_2O$. It is decomposed by water with formation of basic salts, the proportion of acid to base in which depends on the degree of washing to which the precipitate is subjected. By dissolving the oxide in dilute nitric acid, a basic salt crystallising in needles and containing $Hg(NO_3)_2.HgO.H_2O$ is obtained. Mercuric nitrates form a large number of double salts with other mercury compounds.

172. Trimercurous Phosphate, Hg_3PO_4, is a white powder formed by the addition of sodium phosphate to mercurous nitrate solution. It is soluble in excess of mercurous nitrate, and is decomposed on boiling into mercuric phosphate and metallic mercury.

Trimercuric Phosphate, $Hg_3P_2O_8$, is obtained by mixing solutions of sodium phosphate and mercuric nitrate. It is a white powder, soluble in ammonium chloride. It melts to a clear yellow liquid, and is decomposed by alkalies and alkaline carbonates.

173. A basic **mercuric carbonate** of a reddish-brown colour and of the composition $HgCO_3.3HgO$ is formed by adding sodium carbonate to a solution of mercuric nitrate. **Mercurous carbonate**, Hg_2CO_3, is an unstable substance formed by adding sodium hydrogen carbonate to solution of mercurous nitrate.

174. **Mercurammonium Salts.**—By the action of ammonia or ammonium salts mercury compounds yield a variety of bodies, some of which have long been used in medicine. They may be regarded as ammoniacal derivatives, in which the hydrogen is replaced by an equivalent of mercury.

Mercuroso-ammonium Chloride, NH_3HgCl or $N_2H_6Hg_2Cl_2$, is formed by the action of ammonia gas on dry calomel. On adding calomel to aqueous ammonia **di-mercuroso-ammonium chloride**, NH_2Hg_2Cl, is formed. The corresponding nitrate, $2(NH_2Hg_2.NO_3).H_2O$, forms, according to Kane, the chief constituent of the soluble mercury of Hahnemann. According to C. G. Mitscherlich this substance has the composition of **trimercuroso-ammonium nitrate**, $NHHg_3NO_3.H_2O$.

Mercuro-diammonium Chloride, $N_2H_6HgCl_2$, constitutes the *fusible white precipitate* of pharmacy, and is formed by adding a solution of corrosive sublimate to a hot solution of sal-ammoniac and ammonia so long as the precipitate first formed redissolves. On cooling, the compound separates out in dodecahedrons. **Mercurammonium chloride**, NH_2HgCl, the *infusible white precipitate* of pharmacy, is obtained by the addition of ammonia to solution of mercuric chloride. By long contact with water it is gradually converted into **di-mercurammonium chloride**, $NHg_2Cl.H_2O$.

The corresponding iodine compound, $NHg_2I.H_2O$, is a reddish-brown powder formed by heating mercuric iodide with ammonia:

$$2HgI_2 + 4NH_3 + H_2O = NHg_2I.H_2O. + 3NH_4I,$$

or by adding ammonia to a solution of the iodide in potassium iodide (potassio-mercuric iodide) made alkaline with potash,

$$2(2KI.HgI_2) + NH_3 + 3KHO = NHg_2I.H_2O. + 7KI + 2H_2O.$$

This alkaline liquid, known as Nessler's fluid, constitutes an exceedingly delicate test for ammonia.

When dry ammonia gas is passed over yellow mercuric oxide, **trimercuro-diamine**, N_2Hg_3, is formed.

$$2NH_3 + 3HgO = N_2Hg_3 + 3H_2O.$$

It may be regarded as formed from 2 molecules of ammonia by the replacement of the 6 hydrogen atoms by 3 atoms of dyad mercury. It is a dark-brown highly explosive powder. If the precipitated oxide be treated with aqueous ammonia **mercurhydroxylamine**, NHg_2OH, is formed. It is perfectly stable, and dissolves in acids forming salts.

The substance formerly known as *ammoniacal turpethum* is a di-mercurammonium sulphate, $(NHg_2)_2SO_4.2H_2O$, formed by the action of ammonia on mercuric sulphate.

Mercury compounds are volatilised on heating, some of them without decomposition, others with the formation of the metal. In the reducing area of the Bunsen flame, or when heated with sodium carbonate in a tube, they readily yield the metal. In acid solutions, copper becomes coated with a lustrous deposit of mercury.

Mercurous salts in solution give a white precipitate of calomel with hydrochloric acid, becoming black on treatment with ammonia, from the formation of di-mercuroso-ammonium chloride, NH_2Hg_2Cl; sulphuretted hydrogen yields a mixture of metal and mercuric sulphide. Potassium iodide gives a greenish-yellow precipitate of mercurous iodide, soluble in excess of the precipitant.

Solutions of mercuric compounds give no precipitate with hydrochloric acid; sulphuretted hydrogen yields a precipitate which, with solutions of the haloid mercuric salts, is first white, then yellow, next orange, and ultimately black. These changes of colour are due to the formation of sulphohaloid salts, *e.g.*, $HgCl_2.2HgS$, which are eventually entirely converted into mercuric sulphide by the continued action of the sulphuretted hydrogen. Potassium iodide gives a yellow precipitate of mercuric iodide which rapidly changes to scarlet; it is readily soluble in excess either of potassium iodide or of mercuric salt.

CHAPTER VII.

GROUP III.—TRIAD METALS.

Antimony.	?Gallium
Bismuth.	Indium.
Yttrium.	Rhodium.
Didymium.	
Erbium.	Gold.

Antimony and bismuth are closely related to the phosphorus group of non-metals; the former metal, indeed, stands in the same relation to arsenic and phosphorus that tellurium stands to selenium and sulphur, or in which iodine stands to bromine and chlorine. Arsenic has an atomic weight which is nearly the arithmetic mean of the atomic weights of phosphorus and antimony:

$$\frac{31+122}{2} = 76{\cdot}5;$$

the atomic weight of antimony is approximately equal to the mean of the atomic weights of phosphorus and bismuth:

$$\frac{31+210}{2} = 120{\cdot}5^{*}.$$

The chemical analogies of yttrium, didymium, erbium, cerium, and lanthanum have been much discussed, but their position among the groups is still doubtful. It appears to be highly probable that these metals are not dyads as hitherto supposed: according to Cleve, their lowest oxides possess the general formula M_2O_3. Mendelejeff has, independently,

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* The atomic weight of antimony is not known with certainty. The value given in this work is founded on the independent experiments of Dumas, Kessler, and Dexter. Schneider, and also Rose, obtained 120·3; Weber, 120·7. It is worthy of note that the mean of these last numbers agrees exactly with the mean of the atomic weights of P and Bi; and by using this atomic weight we also obtain a closer approximation to the atomic weight of arsenic than that given above, viz.:

$$\frac{31+120{\cdot}5}{2} = 75{\cdot}75.$$

arrived at the same conclusion from considerations based upon his laws of periodicity (p. 32). Lanthanum and didymium, although frequently occurring together, are not strictly analogues, and the corresponding salts of the two metals are not isomorphous. The sulphates of yttrium, didymium, and erbium, however, possess the same crystalline shape, and may be represented by the general formula $M_2(SO_4)_3.8H_2O$. The atomic weight of didymium (138) approximates to the mean of the atomic weights of yttrium and erbium: the exact values are, however, unknown on account of the great difficulty in preparing perfectly pure salts of the respective metals.

Very little is yet known of the recently-discovered metal gallium, the existence of which was detected by M. Lecoq de Boisbaudran in the zinc blende of Pierrefitte (Pyrenees) by the aid of spectral analysis. The salts of gallium appear to possess the general formula GaX_3; its oxide being Ga_2O_3; it also forms an alum. The metal has a bluish-white colour, and crystallises in octahedrons; it is not readily oxidised even at moderately high temperatures, but it is easily acted upon by dilute acids. It melts at 30·1°, and has a specific gravity of 5·95. In several respects gallium is analogous to indium; it may possibly bear the same relation to this element that zinc bears to cadmium. It forms a white sulphide, and its oxide is soluble in potash.

From its analogy to zinc and cadmium, indium was formerly regarded as a dyad, its equivalent being assumed to be 37·8, and its atomic weight 75·6. Mendelejeff, however, predicated that the metal was in reality triadic, its oxide having the formula In_2O_3, and its chloride that of $InCl_3$; hence the atomic weight would be $37·8 \times 3 = 113·4$. The determination of the specific heat of the metal by Bunsen has confirmed this supposition. According to Bunsen, the specific heat of indium is 0·57, which number, multiplied by 75·6, gives 4·3 as the atomic heat, a result which does not agree with Dulong and Petit's law. By taking the atomic weight as $1\frac{1}{2}$ times 75·6, the atomic heat becomes 6·5, or very nearly that required by the law.

Rhodium is usually regarded as a tetrad, and is classed with platinum and its congeners. It forms, however, but one chloride, $RhCl_3$, and its sulphate has the formula $Rh_2(SO_4)_3.12H_2O$. Moreover, its ammoniacal derivatives are best represented on the assumption that it is triadic.

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175. Antimony—Symbol Sb (Stibium); atomic weight, 122 (120·5 ?).—The main properties of this metal were described by Basil Valentine as early as 1490. It is found in the free state associated with arsenic, nickel, and silver; but it is generally obtained by heating the trisulphide with metallic iron, or by roasting this mineral to an oxide and reducing it with charcoal and sodium carbonate.

In the direct extraction of the metal from the sulphide the ore is usually first heated on the inclined hearth of a reverberatory furnace, or in pots standing on receivers; the sulphide melts and flows from the admixed "gangue," and is thus obtained free from siliceous and earthy matters: this process is known as *liquation*. Fig. 142 represents a liquation furnace used in France: the ore is introduced into the cylinders *aa*, which stand on perforated plates, and the melted sulphide collects in the pots *bb*. The *crude antimony*, as the product is termed, contains about 60 per cent. of the metal, with more or less arsenic, lead, and iron: to obtain the antimony the sulphide is then heated to redness with scrap iron in covered crucibles placed in a reverberatory furnace, when the following reaction occurs: $Sb_2S_3 + 3Fe = 3FeS + Sb_2$.

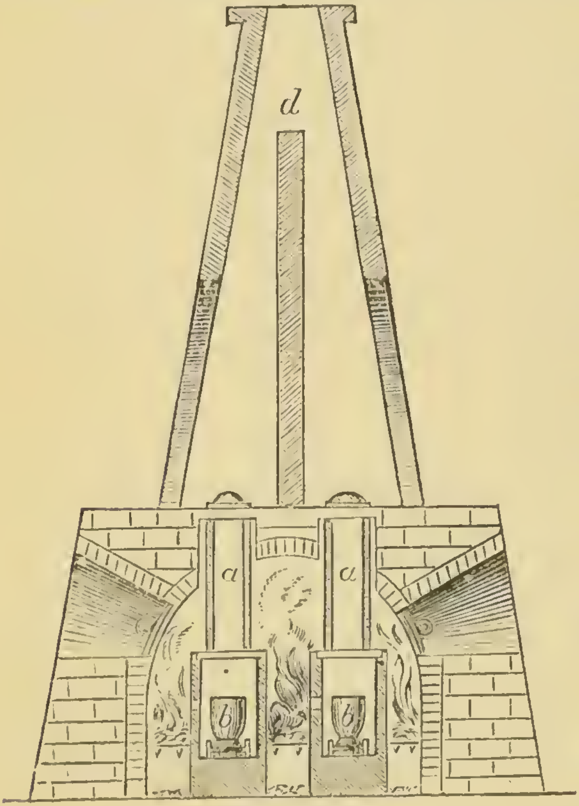


Fig. 142.

The metal is fused with sodium carbonate and charcoal in order to remove the greater portion of the foreign metals, and is cast beneath melted tallow or under a readily fusible slag.

The commercial metal often contains considerable quantities of arsenic, sulphur, iron, and lead. Antimony shows a considerable tendency to crystallise, and as sent into commerce it frequently exhibits beautiful fern-shaped markings upon its surface. By melting a quantity of the metal, it may be obtained in rhombohedral crystals. Antimony has a bluish-white colour; it is very brittle, and may easily be reduced to powder in a mortar. Its density is 6·8. It melts at 450°, and may be distilled at a high temperature in a current of hydrogen.

Pure antimony is permanent in the air at ordinary temperatures: when melted it oxidises, and at a red heat takes fire and burns with a white flame, forming the trioxide.

Antimony is deposited by the electrolysis of a solution of tartar emetic in antimony chloride as a highly-lustrous amorphous metal of specific gravity 5·78. When struck, the amorphous metal becomes very hot, chloride of antimony and hydrogen (?) are evolved, and it is changed into the ordinary variety.

Antimony is mainly used in the arts for alloying with other metals. *Type-metal* is an alloy of antimony and lead containing about 20 per cent. of the former metal. *Stereo-metal* is an alloy of tin, lead, and antimony. Alloys of tin, lead, and antimony, and occasionally copper, are used for machinery bearings. Antimonide of nickel, NiSb, is found native as the mineral *breithauptite*, and antimonide of silver as *dicrasite*, Ag_4Sb.

176. **Antimony Hydride** or **Stibine**, SbH_3, is best obtained by dissolving an alloy of zinc and antimony in dilute hydrochloric or sulphuric acid. It is impossible to obtain it free from admixed hydrogen. It is a colourless, odourless gas, which takes fire on the approach of a light, and burns with a bluish-white flame, forming antimony trioxide and water. When passed through solutions of silver or mercury it forms black precipitates: the composition of the silver compound is Ag_3Sb. If the gas be passed through a red-hot tube, metallic

antimony is deposited as a smoky black film possessing but little lustre. The film of antimony is distinguished from that of arsenic, obtained by the decomposition of arsenic trihydride, by its insolubility in solutions of the hypochlorites.

177. **Antimony Trioxide**, Sb_2O_3, is found native as *valentinite*, which occurs in rhombic prisms; and (although more rarely) as *senarmontite*, which crystallises in regular octahedrons. The trioxide is, therefore, isodimorphous with the corresponding oxide of arsenic. It may be formed artificially by the combustion of the metal in air, or by the action of steam upon the metal at a high temperature:

$$Sb_2 + 3H_2O = Sb_2O_3 + 3H_2.$$

It is also obtained by mixing hot solutions of antimony trichloride and sodium carbonate. It is a greyish-white powder which becomes temporarily yellow on heating; it melts at a red heat, and may be sublimed unchanged out of contact with air: by exposure to oxygen when heated it forms the tetroxide. It is soluble in cream of tartar, forming *tartar emetic*, $C_4H_4O_6\left.\right\}\begin{matrix}K\\SbO\end{matrix}$, and in hydrochloric acid to form the trichloride.

178. **Antimony Tetroxide**, Sb_2O_4, or **antimony antimonate**, $Sb_2O_3.Sb_2O_5$, is obtained by roasting the preceding compound, or by the action of nitric acid upon the metal. It is found native as *antimony ochre*. It is a white powder, easily soluble in hydrochloric acid. When treated with a hot solution of acid potassium tartrate (cream of tartar), antimony pentoxide remains undissolved whilst the trioxide passes into solution forming tartar emetic.

179. **Antimony Pentoxide**, Sb_2O_5, is best obtained by heating the finely-powdered metal with mercuric oxide. It is a light-yellow powder of specific gravity 6·6, insoluble in water and in acids. When strongly heated, it is converted into antimony antimonate.

Antimony pentoxide is also obtained by the dehydration of antimonic acid.

180. **Antimonic Acid**, $HSbO_3$, exists in two modifications distinguished by different basicities. Antimonic acid obtained by the action of nitric acid upon the metal, or by adding an

acid to a solution of potassium antimonate, is a white powder very slightly soluble in water, and almost insoluble in ammonia. It gives rise to a series of neutral salts possessing the general formula $MSbO_3$. **Metantimonic acid** is obtained by the decomposition of antimony pentachloride by water. It is more soluble in water than antimonic acid, and is readily dissolved by ammonia. It is dibasic, forming unstable salts of the general formula $M_4Sb_2O_7$ and $M_2Sb_2O_5$. The alkaline metantimonates are crystalline, whereas the antimonates are amorphous. The soluble acid-metantimonates give a precipitate with a sodium salt: the soluble antimonates give no such precipitate (see Vol. I., p. 80). By adding nitric acid to a solution of potassium antimonate, washing the precipitate, and allowing it to dry by exposure to air for many months, a hydrate of the formula H_3SbO_4, corresponding to arsenic and phosphoric acids, is obtained. On heating to 175° it loses water, and is converted into the ordinary acid $HSbO_3$. Fremy obtained a third hydrate of the composition H_5SbO_5. A basic lead antimonate is used as a pigment under the name of *Naples yellow.* The acid-metantimonate of potassium, $KHSbO_3.3H_2O$, is occasionally used as a test for sodium compounds, with which it forms a precipitate of the composition $NaHSbO_3.3H_2O$.

181. **Antimony Trichloride**, $SbCl_3$, is obtained by the action of chlorine or mercuric chloride upon the metal, or by heating the trisulphide with mercuric chloride. It is a translucent light-yellow fatty mass, whence its common name of *butter of antimony;* it melts at 72°, and boils at about 223°; it is decomposed by water with the formation of the trioxide and hydrochloric acid, and two insoluble oxychlorides, viz., $Sb_4O_5Cl_2$, crystallising in monoclinic prisms, formerly known as *powder of Algaroth;* and SbOCl or **stibyl monochloride.**

The **pentachloride**, $SbCl_5$, is formed by heating the metal with an excess of chlorine, or by passing chlorine into the trichloride. It is a yellow, fuming, volatile liquid, freezing at − 6°, and decomposing on boiling into the trichloride and free chlorine. From the ease with which this decomposition occurs, the pentachloride is frequently employed as a chlorinating agent. It is decomposed by water yielding hydro-

[illegible]

chloric and antimonic acids. By the cautious addition of absolute alcohol, it yields an alcoholate of the composition $SbCl_5.C_2H_6O$; this compound crystallises in white rhombic prisms; it is hygroscopic, melts at about 67°, and is freely soluble in alcohol, ether, and chloroform. It is not very stable, and is at once decomposed by water with the formation of alcohol, antimonic and hydrochloric acids. Similar compounds are obtained with methyl and amyl alcohols, and with ordinary ether. (Williams.)

An **oxychloride**, $SbOCl_3$, and a **thiochloride**, $SbSCl_3$, analogous to the corresponding phosphorus compounds, are also known. Two oxychlorides, $Sb_3Cl_{13}O$, melting point 85°, and $Sb_3Cl_7O_4$, melting point 97·5°, have been obtained by W. C. Williams by heating the pentachloride with the pentoxide (obtained by decomposing the pentachloride with water). The former body may be regarded as derived from a triple molecule of the pentachloride by the replacement of Cl_2 by O; in the latter compound, 4 atoms of oxygen have replaced 8 of chlorine in the original triple molecule.

182. Antimony Tribromide, $SbBr_3$, the only known compound of bromine and antimony, is formed by the direct union of its elements; it is a colourless, crystalline, deliquescent body, melting at 90° and distilling at 270°. It is soluble in carbon bisulphide, and is decomposed by water, forming an oxybromide.

183. Antimony Tri-iodide is a dark-red crystalline body obtained by shaking finely-powdered antimony with a solution of iodine in carbon disulphide. It forms a series of richly-coloured double salts with the iodides of the alkalies and alkaline earths.

An orange-coloured **sulphiodide**, $Sb_2S_3I_2$, is formed together with the tri-iodide, by heating the trisulphide with iodine.

184. Antimony Trifluoride, SbF_3, is obtained by dissolving the trioxide in hydrofluoric acid. It is a white, crystalline, deliquescent salt, soluble in water without the precipitation of the trioxide. It unites with alkaline fluorides, forming double salts, which decompose when heated in contact with air.

Antimony Pentafluoride, SbF_5, is obtained by dissolving antimonic acid in hydrofluoric acid: the solution on evaporation *in vacuo* leaves the compound as an amorphous mass. It combines with the alkaline fluorides, giving rise to a well-crystallised series of salts.

185. **Antimony Trisulphide**, Sb_2S_3, is found native as the mineral *stibnite* or *antimony-glance*, and is the principal ore of the metal. It is found in Germany, France, Cornwall, America, etc., in well-defined prisms belonging to the rhombic system. It has a leaden-grey colour and metallic lustre, and is readily fusible. It is obtained of a reddish colour by throwing it when fused into water: thus treated, it is destitute of crystalline form. The amorphous hydrated sulphide is readily obtained of a dark-orange colour by passing sulphuretted hydrogen through an acidulated solution of the trichloride, or through a solution of tartar emetic containing acetic acid. On heating to about 200° it parts with its water, turns black, and fuses, forming the grey sulphide. At a few degrees above its melting point it takes fire and burns with a blue flame. It is soluble in alkaline sulphides, forming salts termed **sulphantimonites** (so-called *livers of antimony*). A number of sulphantimonites of the heavy metals occur native, *e.g.*, *Boulangerite* $Pb_3(SbS_3)_2$, *Berthierite* $Fe(SbS_2)_2$, and the various *fahl-ores*.

The **pentasulphide**, Sb_2S_5, is obtained as a yellowish-red amorphous powder by passing sulphuretted hydrogen through a solution of the pentachloride in water containing tartaric acid. It is readily soluble in alkaline hydrates and sulphides, forming salts termed **sulphantimonates**, the best known of which is *Schlippe's salt*, the **sodium sulphantimonate**, $Na_3SbS_4.9H_2O$. This body unites with sodium thiosulphate to form a double salt of the composition

$$3Na_2S.Sb_2S_5.2(Na_2O.S_2O_2).40H_2O.$$

It is interesting from the fact that it contains more molecules of water than any other inorganic salt at present known.

The pharmaceutical preparation known as *sulpho-stibias-calcius* is a mixture of the calcium salt with excess of lime and antimony oxysulphide. The so-called "red antimony," a mineral of a dark-red colour, consists of **antimony oxysulphide**,

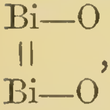
$Sb_2O_3.2Sb_2S_3 = Sb_2OS_2$. It may be obtained artificially by fusing the trioxide with antimony trisulphide.

Antimony is readily recognised by its orange-coloured sulphide, insoluble in dilute hydrochloric acid, but soluble in alkaline sulphides and carbonates. Potash gives a white precipitate of the hydrated oxide, soluble in large excess. Antimony is precipitated from its solutions by iron and zinc as a black powder; by copper as a brilliant metallic film, soluble in solution of potassium permanganate.

207·5

186. Bismuth—Symbol Bi; atomic weight 210.—This element was mentioned by Agricola in 1530, although it was doubtless known before his time. It is found in the metallic state in Saxony, and, associated with sulphur, copper, and lead, in Cornwall and Cumberland. The metal was formerly obtained by heating the impure native bismuth and accompanying gangue in iron tubes placed in an inclined position in a furnace. The bismuth readily fused and ran down the iron tubes into earthen pots, from which it was ladled and cast in moulds. In the process now generally employed, the ore is first roasted, in order to expel any admixed sulphur, and is then melted with charcoal and metallic iron (to remove the last traces of sulphur) beneath slag in crucibles. The bismuth is separated from the slag, which is mixed with an impure *speiss* (produced from the accompanying metals, viz., cobalt and nickel), and is slowly heated on an inclined iron-plate; the readily-fusible bismuth flows away from the foreign metals, and solidifies in hemispherical drops. The metal is further purified by remelting it with a small quantity of nitre, whereby the remaining traces of the copper, iron, sulphur, etc., are oxidised, and collect as a slag on the surface of the bismuth.

Bismuth has a greyish-white colour, and is exceedingly brittle from its highly crystalline nature. When a quantity of the metal is melted in an iron pot, allowed partially to solidify, and the still liquid portion poured away, the sides of the pot are found to be lined with aggregations of rhombic crystals possessing a beautiful iridescent lustre. The metal has a specific gravity of 9·93, but its density is lessened by subjecting it to intense pressure. Bismuth melts at 264°, and expands on solidifying. It is permanent in the air, but when heated it oxidises with the formation of a dioxide Bi_2O_2



$\begin{array}{l}\mathrm{Bi—O}\\ \| \\ \mathrm{Bi—O}\end{array}$

, and eventually takes fire and burns with a blue flame, forming the trioxide. It is but slowly attacked by hydrochloric and sulphuric acids, but is readily dissolved by nitric acid. Bismuth is the most diamagnetic of the metals.

Bismuth is principally used for alloying with other metals. *Fusible metal* consists of 2 parts of bismuth, 1 of lead, and 1 of tin. When heated, this alloy expands regularly up to 60°, when it contracts until it melts at 95° to 98°, after which it again expands: 1 volume at 0° becomes 1·00267 volumes at 60°; at 82° it again becomes 1 volume; at 95° its volume is 0·9947. This property of expanding when cooling renders the alloy very valuable for taking impressions from dies, etc., as even the faintest lines are faithfully reproduced.

187. Bismuth Trioxide, Bi_2O_3, occurs native as *bismuth ochre*, and is formed artificially by heating the metal in air, or by igniting the nitrates. It is a yellow powder, which fuses at a high temperature and solidifies on cooling to a transparent glass. It is obtained as a **hydrate,** $Bi_2O_3.H_2O$ or $BiHO_2$, by adding caustic potash or ammonia to a solution of the nitrate: on boiling with excess of alkali, the precipitate loses water and becomes yellow.

Bismuth Pentoxide, Bi_2O_5, is a red powder formed by passing chlorine into a solution of potash containing the trioxide in suspension, and digesting the product with warm strong nitric acid to remove any admixed trioxide.

Bismuth pentoxide readily parts with a portion of its oxygen on heating, passing into the **tetroxide** Bi_2O_4 or *bismuth bismuthate* $Bi_2O_3.Bi_2O_5$. The strong acids convert it into the trioxide.

Finely-powdered bismuth takes fire when thrown into chlorine gas, forming the **trichloride** $BiCl_3$. It is a white hygroscopic substance, melting at 230°, and volatilising at a higher temperature. It dissolves in dilute hydrochloric acid:

the solution on the addition of water becomes turbid from the formation of **bismuth oxychloride**

$$BiCl_3+H_2O=BiOCl+2HCl.$$

The oxychloride is also formed by adding a solution of bismuth nitrate to a solution of a chloride. It is used as a pigment under the name of "pearl white." An oxychloride of the formula $Bi_2O_3.BiOCl$ is found in Bolivia, in opaque crystalline plates of a pearly lustre; it is known as *daubreite.*

The **dichloride**, Bi_2Cl_4, is formed by heating the trichloride with metallic bismuth. It is a brown fusible substance, decomposed by water, and resolved into bismuth and the trichloride at a high temperature.

188. Bismuth Tribromide, $BiBr_3$, is a golden-yellow crystalline substance, formed by the direct action of bromine upon bismuth: it is soluble in ether, and may be obtained by evaporation in deliquescent prisms. It melts at 215°, and boils at a red heat, giving a red vapour.

The **dibromide**, Bi_2Br_4, is a brown solid obtained by heating the tribromide with metallic bismuth.

189. Bismuth Tri-iodide, BiI_3, may be obtained by the action of iodine upon bismuth or upon the trisulphide. It crystallises in large grey-coloured six-sided plates. On heating in contact with air it forms a red **oxyiodide**, $BiOI$. On treating the tri-iodide with sulphur it is converted into the **sulphiodide** $BiSI$, which crystallises in steel-grey needles. A corresponding sulphochloride and selenochloride are known.

The **trisulphide**, Bi_2S_3, is found native as *bismuth-glance*, and may be prepared artificially by fusing bismuth with sulphur, or as a dark-brown precipitate by passing sulphuretted hydrogen through a solution of a bismuth salt. The **disulphide**, Bi_2S_2, is formed by fusing the preceding compound with bismuth. It forms needle-shaped crystals of a high metallic lustre and steel-grey colour. An **oxysulphide**, Bi_4O_3S, occurs native as the mineral *karelinite.*

The normal **nitrate**, $Bi(NO_3)_3.5H_2O$, is obtained by the direct action of the acid upon the metal. It forms large, colourless, deliquescent crystals, which are decomposed by water with the production of a basic salt $Bi(NO_3)_3.Bi_2O_3.3H_2O$. Several other basic nitrates are known.

Bismuth salts in solution give a dark-brown precipitate of the hydrated sulphide, Bi_2S_3, with sulphuretted hydrogen: this substance is insoluble in ammonium sulphide, but readily soluble in nitric acid. Ammonia yields a white precipitate of the hydrate: on dissolving this precipitate in the least possible quantity of hydrochloric acid, and adding a quantity of water to the solution, bismuthyl chloride, $BiOCl$, is precipitated.

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190. Yttrium—Symbol Y; atomic weight 88?—The existence of this element was first indicated by Gadolin in 1794, in *ytterbite* or *gadolinite*, a rare mineral occurring at Ytterby in Sweden. The pure metal has not yet been prepared: the greyish-black lustrous powder obtained by the action of potassium upon the impure chloride, and considered by Berzelius to be yttrium, was a mixture of that metal with erbium.

The **oxide**, Y_2O_3, is a white powder obtained by heating the hydrate formed on adding caustic potash to solutions of yttrium salts. It glows when ignited, but its spectrum is free from bright bands; its solutions, moreover, do not exhibit absorption bands.

The **chloride**, $YCl_3.6H_2O$, is a deliquescent body obtained by dissolving the oxide or hydrate in hydrochloric acid: on heating it loses water, but is not volatile. The **fluoride** occurs in *yttrocerite*, a mineral found in Sweden and North America.

The **sulphate**, $Y_2(SO_4)_3.8H_2O$, is isomorphous with the corresponding salts of didymium and erbium: it forms soluble double salts with the alkaline sulphates.

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191. Didymium—Symbol D; atomic weight 138? (142·5 Hermann, Zschiesche, Erk).—This element was discovered by Mosander in 1841. It occurs associated with yttrium, erbium, cerium, and lanthanum in *cerite*, *yttrocerite*, and other rare minerals. The metal is obtained by the action of potassium on the chloride, and is described as a grey powder, which oxidises even in dry air, and, when finely-divided, decomposes water; it is readily soluble in hydrochloric acid with evolution of hydrogen.

The **oxide**, D_2O_3, is a white powder, soluble in acids. A higher oxide is supposed to exist, but its composition is unknown.

The **chloride**, $DCl_3.6H_2O$, is obtained in rose-coloured crystals by concentrating a solution of the oxide in hydrochloric acid: by heat it is converted into an **oxychloride** of the composition $D_2O_2Cl_2.3H_2O$ (?).

The **sulphate**, $D_2(SO_4)_3.8H_2O$, forms sparingly soluble double salts with the alkaline sulphates of the general formula $DM(SO_4)_2$. The ammonium salt crystallises with 4 molecules of water, and corresponds to the indium-ammonium-sulphate $InAm(SO_4)_2.4H_2O$, crystallised at 36°. Didymium sulphate is more soluble in cold than in hot water.

Solutions of didymium salts possess a rose or violet colour: they afford a remarkable absorption spectrum, first observed by Gladstone. The number of the absorption-bands increases with the concentration of the solution, one in the yellow and one in the green are especially characteristic; by means of these bands the smallest trace of didymium may be detected in a solution. By comparing their intensity with that of the bands afforded by a didymium solution of known strength, an approximate estimate of the quantity of the element contained in the liquid may be obtained.

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192 Erbium—Symbol E; atomic weight 178?—This element is found associated with yttrium in *gadolinite*, and was discovered by Mosander in 1843. He also announced the existence in this mineral of a third element called *terbium*, but subsequent investigators have failed to recognise it.

The metal erbium has not been obtained. Its **oxide**, E_2O_3, has a light rose-red colour, and when ignited glows with an intense green light, affording a bright band spectrum. The **chloride** and **sulphate** are analogous to the corresponding salts of yttrium and didymium: their solutions give dark absorption-bands coincident with the bright lines afforded by the incandescent oxide. The spectra are perfectly distinct from those of didymium.

193. Indium—Symbol In; atomic weight 113·4.—This rare metal was discovered in 1863 by Reich and Richter by the aid of the spectroscope. It occurs associated with zinc in blende to the extent of from ·006 to 0·1 per cent., and is best obtained from the crude metal or "spelter." It is a silver-white, soft, ductile metal of specific gravity 7·4. It melts at 176° and oxidises at a high temperature, burning with a violet flame, which in the spectroscope exhibits characteristic lines in the violet and blue.

194. Indium Sesquioxide, In_2O_3, is obtained as a light yellow powder by igniting the hydrate or the nitrate. The **hydrate,** InH_3O_3, is formed by adding ammonia to a boiling solution of an indium salt. By igniting the sesquioxide in hydrogen it becomes green, then grey, and ultimately black. The green oxide has the composition $2InO.In_2O_3$, the grey oxide $3InO.2In_2O_3$, and the black oxide InO_2.

195. Indium Chloride, $InCl_3$, is obtained by the direct union of its elements. The metal heated in chlorine burns with a greenish-yellow flame forming white laminæ of the chloride, volatile at a high temperature. It forms double salts with the alkaline chlorides: the ammonium salt has the composition $2NH_4Cl.InCl_3.H_2O$.

196. Indium Nitrate, $In(NO_3)_3$, is obtained by dissolving the metal in nitric acid. The **sulphate,** $In_2(SO_4)_3 9H_2O$, is a non-crystalline powder readily soluble in water, and forming with ammonium sulphate, **indium-ammonium-alum,** $In_2(NH_4)_2(SO_4)_4 + 24H_2O$, crystallising in large octahedrons modified by the cube. It fuses at 36°, breaking up into a solution of the alum, and a salt containing only 4 or 8 molecules of water.

197. Indium Sulphide is a yellow or brown powder formed by passing sulphuretted hydrogen through a neutral solution of an indium salt, or by heating the oxide with sulphur. It is insoluble in colourless solutions of the sulphydrates, but dissolves in yellow ammonium sulphide, and is decomposed by sulphuric and hydrochloric acids.

Indium may be recognised in commercial zinc by treating the metal with hydrochloric acid until the whole is nearly dissolved, pouring off the clear solution and treating the residue with a few drops of sulphuric acid, evaporating nearly to dryness, filtering from any lead sulphate, mixing with excess of ammonia, collecting the precipitate, redissolving it in a small quantity of hydrochloric acid, and adding to the solution acid-sodium sulphite. A salt of the composition $2In_2O_3.3SO_2.8H_2O$ separates out, which readily gives the characteristic spectral indications.

198. **Rhodium**—Symbol Rh; atomic weight 104.—This metal was discovered by Wollaston, in 1804, in certain platinum ores from Brazil: it is always present in greater or less quantity in the residues obtained in the extraction of platinum.* Rhodium resembles platinum in its lustre, but it is harder, less ductile, and more infusible than that metal. When melted it absorbs oxygen, which is partially evolved as the metal solidifies. Its specific gravity is about 12. It is much less permanent in the air than platinum, and at a bright red heat it oxidises. It is almost insoluble in aqua-regia unless alloyed with other metals, but it may be obtained in solution as the sodium chlororhodiate, $3NaCl.RhCl_3$, by igniting a mixture of rhodium and common salt in a stream of chlorine gas.

Rhodium combines with oxygen in four proportions to form RhO, Rh_2O_3, RhO_2, and RhO_3.

The **monoxide** is a dark-grey powder, formed by heating the trihydrated sesquioxide $Rh_2O_3.3H_2O$.

The **sesquioxide** is obtained by heating the nitrate, or as the hydrate $Rh_2O_3.3H_2O$ or RhH_3O_3, by adding strong solution of potash to sodium chlororhodiate.

The **dioxide** is a brown powder obtained by heating the finely-divided metal or the preceding oxide with nitre. It may be obtained hydrated of the composition $RhO_2 2H_2O$, or of a green colour by treating the trihydrated sesquioxide with chlorine.

The **trioxide** is a blue powder produced by passing chlorine into potash solution containing the hydrated sesquioxide in suspension. It readily loses oxygen and is converted into the dioxide.

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* See Bunsen. Phil. Mag. [4], XXXVI., 253.

Rhodium appears to form only one combination with chlorine, viz., the **trichloride**, $RhCl_3$. It is obtained by heating the metal in chlorine, or by treating sodium chlororhodiate with sulphuric acid. It is a brownish-red powder, insoluble in water, acids, and alkalies. In the hydrated state $RhCl_3.4H_2O$, as obtained by concentrating a solution of rhodic oxide in hydrochloric acid, it is readily soluble in water and alcohol. This compound combines with alkaline chlorides to form double salts, termed **chlororhodiates**, of a dark-red or rose colour, whence the name of the element. When the ammoniacal compound is mixed with excess of ammonia, the solution filtered and concentrated, a yellow salt is obtained, which, on treatment with water, loses ammonium chloride and forms **ammonio-rhodium trichloride**, $5NH_3.RhCl_3$. This compound is the *chloride of a rhodamine*, the oxide of which $10NH_3.Rh_2O_3$, may be obtained by digesting the salt with silver oxide and water.

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199. Gold—Symbol Au (Aurum); atomic weight 197.—Gold has been known from very early times: its comparative rarity, its exceptional colour, and its power of resisting atmospheric influences have caused it to be esteemed as one of the most precious of metals. By the alchemists it was known under the symbol of the sun, ☼. Although seldom met with in large quantity in any one locality, it is one of the most widely-distributed of the elements. It is chiefly found in the metallic state, and generally alloyed with more or less silver, copper, and iron: the following analyses will serve to show the general composition of the native metal:

	Australia.	California.	Russia.	Wales.
Gold,	94·64	89·10	98·96	89·83
Silver,	4·95	10·50	0·16	9·24
Copper,	—	—	0·05	—
Iron,	0·41	0·20	0·35	—
	100·00	99·80	99·52	99·07

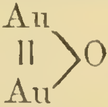
Gold has been hitherto met with in largest quantity in alluvial deposits formed by the disintegration of crystalline, metamorphic, and trachytic rocks; hence the sands of many rivers contain it in notable amount. The chief supplies of the metal are now obtained from California, Australia, and British Columbia, although in former times Spain, Hungary, the Indies, and South America furnished considerable amounts. In order to extract the gold from alluvial deposits, advantage is taken of its high specific gravity. The auriferous earth is washed in a stream of water whereby the siliceous particles are carried away, and the greater portion of the metallic grains remains at the bottom of the washing apparatus.

In Australia and in America considerable quantities of gold are found in quartz in filiform and arborescent fragments. The gold-quartz is crushed between iron rollers, or stamped to coarse powder by means of heavy hammers. The gold in the crushed ore is then extracted by mercury, and the amalgam is distilled to separate the metals. Molten lead, which readily dissolves gold, is sometimes employed instead of mercury, the metals being afterwards separated by cupellation. The gold obtained in these processes invariably contains more or less silver and copper: the last-named metals are separated from the gold by the process termed *quartation* or *parting*. The alloy is first melted in wrought-iron crucibles and poured into water in order to granulate it. It is then boiled with strong sulphuric acid, whereby the silver and copper are converted into sulphates which dissolve in hot water, and the gold is left behind as a black powder. If the proportion of gold is considerable, the alloy must first be fused with silver before the operation of parting is commenced. The silver is readily obtained from the solution by the addition of scrap-copper. The gold is frequently further purified by forcing chlorine gas through it when molten: the remaining traces of silver rise to the surface as silver chloride, and any arsenic, bismuth, or antimony (which render the metal brittle), are expelled as volatile chlorides.

Gold is one of the few metals possessing a yellow colour. When beaten out into thin leaves and viewed by transmitted light it appears green; when very finely-divided it is dark-red or black. Gold is the most malleable and ductile of the metals: it may be beaten out into leaves not exceeding $\frac{1}{10,000}$th of a millimetre in thickness. Faraday calculated that the gold contained in four sovereigns could be made into a wire long enough to surround the earth. The specific gravity of gold is about 19·3; it melts at about 1300°, and may be volatilised at a high temperature. It preserves its lustre in the air, and is not acted upon by any of the ordinary acids. Chlorine in solution and nitrohydrochloric acid convert it into the trichloride.

Gold alloys readily with other metals. Pure gold is nearly as soft as lead: in order to increase its hardness when used for articles of jewellery and for coinage it is mixed with silver or copper. The alloy employed for coin in this country consists of 11 parts of gold and 1 part of copper: the specific gravity of this alloy is 17·157. In the United States and in France the proportion of the metals is 9 of gold to 1 of copper. The "fineness" of gold, or its proportion in the alloy, is usually expressed by stating the number of carats present in 24 carats of the mixture. Pure gold is stated to to be 24 carats "fine:" sovereign or standard gold is 22 carats "fine:" 18 carat gold is a mixture of 18 parts of gold and 6 of alloy.

The fineness of gold may be approximately estimated by means of the *touch-stone*, a basaltic stone formerly obtained from Asia Minor, but now procured from Saxony and Bohemia. The sample of gold to be tested is drawn across the stone, and the streak of metal is treated with dilute nitric acid: from the rapidity of the action, and the intensity of green colour produced (due to the solution of the copper), as compared with streaks made by alloys of known composition, the assayer is enabled to judge of the proportion of inferior metal which is present.

Gold unites with oxygen in two proportions to form the **monoxide**, Au_2O or  $\left.\begin{array}{c}Au\\ \|\\ Au\end{array}\right\rangle O$, and the **trioxide**, Au_2O_3. The monoxide is a green unstable powder obtained by cautiously adding caustic potash to a solution of the auric chloride. The trioxide is formed by adding an excess of alkali and then sulphurous acid to a solution of the trichloride. It is a brown powder which is decomposed by exposure to light or by heating. It is dissolved by alkalies and forms salts termed **aurates**: the potassium salt has the composition $KAuO_2.3H_2O$: it is very soluble in water, and is used in electro-gilding. On adding potassium sulphite to its solution, **potassium aurosulphite**, $2(KAuO_2.4HKSO_3)H_2O$, is deposited in fine yellow needles; the salt is decomposed on boiling with water. A **sodium-aurous-thiosulphate**, $Na_3Au(S_2O_3)_2.2H_2O$, formed by mixing strong solutions of gold chloride and sodium thiosulphate, is employed in photography.

200. Aurous Chloride, Au_2Cl_2, is a yellowish-white insoluble powder obtained by heating auric chloride to 180° or 200° until the colour changes to pure yellow. It is decomposed by boiling water into metallic gold and the trichloride,

$$3Au_2Cl_2 = 2AuCl_3 + 2Au_2.$$

Auric Chloride, $AuCl_3$, is obtained by dissolving the metal in nitrohydrochloric acid. It is a deep-red crystalline deliquescent powder. The yellow needle-shaped salt usually obtained by evaporating the acid solution to the crystallising point is an acid chloride, $HCl.AuCl_3$. Auric chloride is soluble in ether and in alcohol. It readily unites with other chlorides to form double salts, termed **chloro-aurates.** The potassium compound has the composition $2(KCl.AuCl_3).5H_2O$. Auric chloride also unites with many hydrochlorates of organic bases, *e.g.*, strychnine, ethylamine, etc., to form characteristic compounds.

201. Aurous Iodide, Au_2I_2, is a light-yellow sparingly soluble powder, formed by adding potassium iodide to auric chloride,

$$2AuCl_3 + 6KI = Au_2I_2 + 2I_2 + 6KCl.$$

By carefully adding auric chloride to potassium iodide the dark-green **auric iodide**, AuI_3, may be obtained; it readily decomposes into aurous iodide and free iodine. Auric iodide unites with the alkaline iodides to form compounds termed **iodo-aurates.** The potassium compound $KI.AuI_3$ forms highly lustrous, intensely black four-sided prisms.

202. Aurous Sulphide, Au_2S, is obtained as a dark-brown powder by treating a hot solution of auric chloride with sulphuretted hydrogen. It dissolves in alkaline sulphides to form double salts.

Auric Sulphide, Au_2S_3, is a yellow powder, formed by passing sulphuretted hydrogen into a cold and dilute solution of auric chloride. Neither of these compounds can be obtained pure by the action of sulphuretted hydrogen: the precipitated sulphide invariably contains more or less free sulphur and metallic gold.

A double sulphide of gold and silver, $2\ Au_2S_3.5Ag_2S$, is formed by the action of sulphur upon an alloy of the two metals: it is a dark-grey crystalline substance of specific gravity 8·159, and is decomposed by ignition in hydrogen.

The presence of gold in a mineral may be detected by agitating it in a state of powder with alcoholic tincture of iodine, dipping a piece of Swedish filter-paper into the liquid and incinerating it: the gold is indicated by the purple colour of the ash. The alcoholic tincture should then be evaporated to dryness, heated gently, the residue treated with nitrohydrochloric acid, and the solution again evaporated. On adding water and dipping into the liquid a glass rod moistened with a mixed solution of stannous and ferric chlorides, the formation of a bluish-purple colour (*Purple of Cassius*) confirms the presence of gold.

CHAPTER VIII.

GROUP IV.—TETRAD METALS.

TIN.

ALUMINIUM.
ZIRCONIUM.
CERIUM.
LANTHANUM.

TITANIUM.

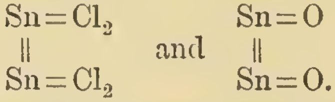
COBALT.
NICKEL.

PLATINUM.
IRIDIUM.

LEAD.

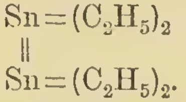
THORIUM.

TIN serves to connect the tetradic non-metallic elements with the above group of metals: it stands to silicon and carbon in the same relation in which antimony stands to phosphorus and nitrogen. Its atomic value is indicated by the tetrachloride and fluoride, by the dioxide, and by stannic ethide, $Sn(C_2H_5)_4$. In certain of its combinations, as in stannous chloride, $SnCl_2$, stannous oxide, SnO, and stannous ethide, $Sn(C_2H_5)_2$, tin appears to be a dyad: the chloride and oxide may, however, be represented as Sn_2Cl_4 and Sn_2O_2: thus



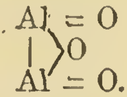
$$\begin{array}{l} Sn=Cl_2 \\ \| \\ Sn=Cl_2 \end{array} \quad \text{and} \quad \begin{array}{l} Sn=O \\ \| \\ Sn=O. \end{array}$$

The molecular weight of stannous ethide is not known, since it cannot be volatilised without decomposition: when vapourised it is resolved into stannic ethide and metallic tin; this fact may possibly indicate that its molecule contains 4 molecules of ethyl and 2 atoms of tin—

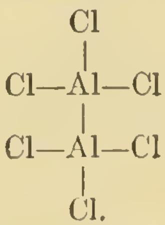


$$\begin{array}{l} Sn=(C_2H_5)_2 \\ \| \\ Sn=(C_2H_5)_2. \end{array}$$

Aluminium is generally regarded as a triad, but some of its compounds appear to be best represented on the assumption that it is tetradic. Alumina, the only known oxide, would thus have the constitution—



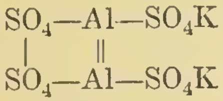
The vapour density of the chloride indicates that its molecule contains 2 atoms of Al; hence its formula may be written—



$$\begin{array}{c} Cl \\ | \\ Cl—Al—Cl \\ | \\ Cl—Al—Cl \\ | \\ Cl. \end{array}$$

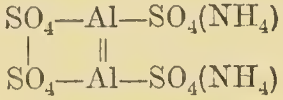
Aluminium methide appears to have a constitution analogous to that of the chloride at temperatures slightly above its boiling point: at 220°, however, its molecule suffers dissociation, yielding 2 molecules of $Al(CH_3)_3$. It is, of course, possible that aluminium, like tungsten and uranium, may have a variable atomicity, being sometimes a perissad, at other times an artiad.

Hertwig and, more recently, Lupton have described a number of potassium-aluminium sulphates, and of ammonium-aluminium sulphates, obtained by the partial dehydration of the corresponding alums: their observations show that the molecule of the common alums must contain, respectively, $Al_2K_2(SO_4)_4$ and $Al_2(NH_4)_2(SO_4)_4$: on the assumption that aluminium is tetradic these compounds would be written—



$$\begin{array}{ccc} SO_4-&Al&-SO_4K \\ | & \| & \\ SO_4-&Al&-SO_4K \end{array}$$

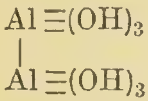
Potash alum.



$$\begin{array}{ccc} SO_4-&Al&-SO_4(NH_4) \\ | & \| & \\ SO_4-&Al&-SO_4(NH_4) \end{array}$$

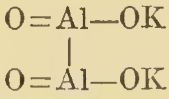
Ammonia alum.

The constitution of a number of aluminium compounds may be expressed as follows:—



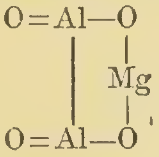
$$\begin{array}{l} Al\equiv(OH)_3 \\ | \\ Al\equiv(OH)_3 \end{array}$$

Aluminium hydrate (*Gibbsite*).



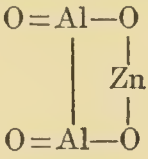
$$\begin{array}{c} O=Al-OK \\ | \\ O=Al-OK \end{array}$$

Potassium aluminate.



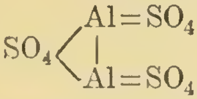
$$\begin{array}{ccc} O=&Al&-O \\ &|&| \\ &|&Mg \\ &|&| \\ O=&Al&-O \end{array}$$

Spinel.

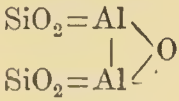


$$\begin{array}{ccc} O=&Al&-O \\ &|&| \\ &|&Zn \\ &|&| \\ O=&Al&-O \end{array}$$

Gahnite.



Aluminic sulphate.



Kaolin.

The tetradic character of zirconium is well marked in its chloride, fluoride, and oxide: this element, indeed, has the closest analogies to silicon and tin.

The relations of cerium, lanthanum, and thorium, have been discussed by Mendelejeff. From considerations based upon his laws of periodicity, Mendelejeff has been led to regard the atomic weight of Ce = 138, that of La = 180, and that of Th = 231·5. The value assigned to Ce agrees with the atomic heat of the metal, as determined by Mendelejeff, and, more recently, by Hillebrand. Cerous oxide has accordingly the formula Ce_2O_3, and ceric oxide that of CeO_2; its two chlorides are respectively Ce_2Cl_6 and $CeCl_4$. The specific heat of lanthanum, according to Hillebrand, is 0·04485, which agrees with the value La = 139 (Cleve). Lanthanum, unlike cerium, forms only one set of compounds, as La_2O_3, La_2Cl_6, and $La_2(SO_4)_3$: in this respect it agrees with thorium, the tetradic character of which has been already pointed out by Chydenius and Delafontaine.

The quantivalence of titanium is indicated by its oxides and chlorides: the dioxide and tetrachloride are strictly analogous to the corresponding compounds of tin and silicon.

Nickel and cobalt are usually associated together by reason of the close resemblance of their derivatives to each other: in the greater number of these compounds the metals appear to act as dyads, but cobalt is distinctly tetradic in its higher oxides, in the oxycobaltamine salts, and in cobaltic chloride.

Platinum and its congener iridium are generally tetrads; although in certain of their compounds they seem to act as dyads; on the whole, however, the general tetratomic character of these metals is more evident than in the case of the other members of the so-called platinum group.

The atomic value of lead is indicated by the constitution of plumbic ethide, $Pb(C_2H_5)_4$, and by that of the unstable tetrachloride, $PbCl_4$: in several of its compounds it is certainly dyadic; in fact, many of its analogies indicate that it stands to the group of the alkaline earths in a relation similar to that in which thallium stands to the alkalies.

203. Tin—Symbol Sn (Stannum); atomic weight 118·10. —This metal, although met with in comparatively few localities, has been known from very early times. The tin mines of Cornwall were worked before the Roman invasion of Britain; indeed, the British Isles were anciently known as the Cassiterides, from the fact of their yielding tin ores (κασσιτερος—tin). The word *stannum* originally denoted any white metallic alloy containing lead or tin: it was only about the fourth century that it was applied solely to the latter metal. By the alchemists tin was known under the sign of Jupiter ♃. Cornwall and Devonshire have long been the principal tin-producing districts of the world. Malacca and Banca also furnish large supplies of the metal; the tin obtained from the latter place is exceptionally pure. A considerable quantity of tin ore is obtained from Saxony, South America, and Australia.

Native tin is exceedingly rare, and has been hitherto met with only in Bolivia. The metal as found in commerce is extracted entirely from "tin stone" or *cassiterite*, SnO_2. The ore is met with in alluvial deposits and in veins accompanied by wolfram and the sulphides of copper, iron, zinc, and arsenic. The rough ore is picked, cleaned, sorted, and crushed to powder, after which it is washed in wooden troughs through which a stream of water flows; the gangue and earthy impurities are carried forward in the stream, and the specifically-heavier ore is gradually concentrated in the residues. The washed ores, containing the oxide of tin and the greater portion of the associated sulphides and wolfram, are then calcined in a reverberatory furnace to expel the sulphur and arsenic, and to oxidise the iron, etc. The roasted mass is next exposed to the air for a short time to convert any sulphides of iron and copper still remaining in the ore into sulphates: these salts are removed by washing, and the copper in solution, if sufficiently large in amount to be worth extraction, is precipitated by means of scrap-iron. The calcined and lixiviated ore is again washed, and if the amount of wolfram is considerable, it is frequently fused with sodium carbonate: sodium tungstate is thus formed, and may be extracted by treatment with water. The tin ore is then mixed with about one-fifth of its weight of powdered anthracite, together with some lime or fluor-spar, and is smelted in a reverberatory furnace (figs. 143 and 144). The reduced metal is then purified, first by *liquation* and then by *lixiviation* or *boiling*. In the operation of liquation the pigs of the crude metal are placed in a reverberatory furnace with a sloping hearth, and are subjected to a temperature sufficiently high to melt out the tin, which flows down the hearth into the refining basin at the bottom, leaving the iron, copper, etc., as oxides in the residuum. The molten tin is next stirred with billets of wood, whereby it is thrown into ebullition by the disengagement of gas from the charring wood: the entangled oxides are thus brought to the surface and are skimmed off. The mass of metal is allowed to cool down gradually: it thus arranges itself into strata of which the upper yields the best quality of tin, the lowest being still very impure. The finer quality is frequently reheated to near the melting point: it

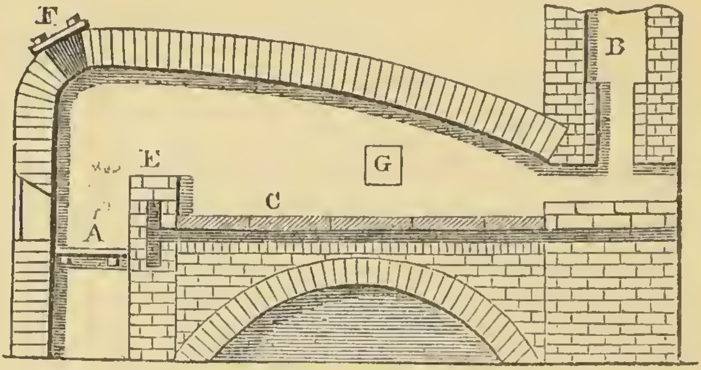


Fig. 143.

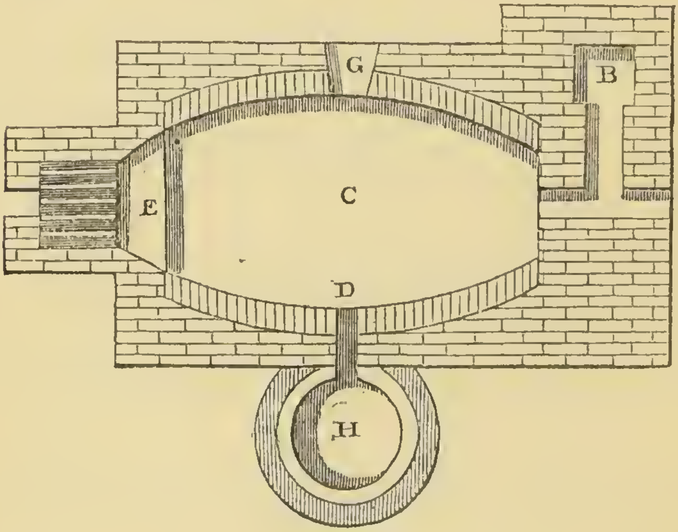


Fig. 144.

thus becomes brittle, and if dropped from a height breaks into prismatic masses, which come into the market as *grain tin*. Commercial tin is seldom free from small quantities of arsenic, lead, copper, iron, etc. To obtain it chemically pure, grain tin is dissolved in hydrochloric acid; a quantity of water is cautiously poured over the strong solution and a bar of tin placed in the liquid, when prismatic crystals of the pure metal are slowly deposited at the juncture of the two layers. Chemically pure tin may also be obtained by reducing the pure dioxide with charcoal prepared from sugar.

Tin is a white, strongly-lustrous metal; when heated it emits a peculiar smell, and when bent gives out a crackling sound, owing to its highly crystalline character. The internal structure of the metal is well seen by washing its surface with dilute aqua-regia: the fern-like appearance of the forms thus developed is due to the reflection of light from the exposed crystals. Large and well-defined crystals may readily be obtained by melting a quantity of the metal, allowing it to solidify partially, piercing the crust, and pouring out the still liquid portion. Tin possesses but little tenacity: it has, however, a high degree of malleability; tin-foil may be obtained in leaves less than $\frac{1}{50}$th of a millimetre in thickness. When exposed to great cold for some time, blocks of tin have been observed to disintegrate in a remarkable manner. The specific gravity of tin varies from 7·14 to 7·3, according to the manner of its preparation and treatment. It melts at about 235°, and boils at a white heat. At ordinary temperatures tin experiences very little change on exposure to air, but in process of time it becomes coated with a dark-brown coating of oxide; when fused in contact with air it acquires a film of oxide; at a white heat it burns with a bright flame, and is converted into the dioxide. The strongest nitric acid has but little action on tin, but in contact with the dilute acid the metal is oxidised with great rapidity; if the acid be cooled the tin dissolves, forming a clear yellow solution; on heating, this liquid becomes colourless, and metastannic hydrate is precipitated. Strong hydrochloric acid quickly dissolves tin on heating, evolving hydrogen and forming stannous chloride. Dilute sulphuric acid has but little action on the metal; when heated with the concentrated acid, sulphur dioxide is evolved.

The alloys of tin are of considerable importance. With copper it forms *gun-metal*, which contains about 10 per cent. of tin. *Bell-metal* contains three parts of copper and one part of tin. *Speculum-metal* usually consists of 1 part of tin and 2 parts of copper: it is white, very hard and brittle, and takes a high polish. *Bronze* is a variable mixture of copper and tin, and often contains zinc, lead, and iron: the bronze employed for the coinage of this country contains 95 parts of copper, 4 parts of tin, and 1 part of zinc. Bronze, by slow cooling, becomes exceedingly brittle and hard: rapid cooling renders it soft. *Solder* is a variable mixture of lead and tin. *Pewter* consists of a mixture of 4 parts of tin and 1 part of lead. *Britannia-metal* and *Queen's-metal* are alloys of tin, copper, zinc, antimony, bismuth, and lead.

Mercury readily dissolves tin, and an amalgam of tin is employed in the manufacture of glass mirrors. A sheet of tin-foil is placed on a smooth stone slab, covered with mercury, and the plate of glass cautiously placed over the surface so that no air-bubbles intervene. Weights are then placed on the glass, and the slab is gradually inclined to allow the excess of the mercury to drain away.

Tin-plate is an alloy of iron and tin formed upon the surface of the former metal. In the manufacture of tin-plate the sheets of iron are carefully cleaned by being immersed for a few minutes in dilute sulphuric acid, placed in a reheating furnace, and when cold hammered and passed between polished rollers to detach any adherent scales of oxide: they are again placed in acid, scoured with bran, and set aside in lime-water (which preserves the surface from oxidation), until wanted. Care is necessary to obtain a perfectly clean surface, otherwise the tin will not alloy with the iron. To coat them with tin, the sheets are placed in a bath of liquid tallow, and they are then immersed in a vessel containing melted tin, in which they remain for a couple of hours. They are next transferred to a second bath of pure tin, and are again heated under tallow to allow the excess of tin to flow down to the edge of the plate. The thick mass of solidified tin is detached from the edge by dipping it into a small quantity of tin, heated considerably above the melting point; by giving the plate a smart blow the excess of the metal is removed. The crystalline appearance known as *moireé metallique,* sometimes given to tin-plate, is obtained by washing it with dilute aqua-regia.

Copper is readily coated with tin by making the surface perfectly clean by rubbing it whilst hot with powdered sal-ammoniac, sprinkling with resin to prevent oxidation, and spreading the melted tin over the plate with tow. Small articles of brass, such as pins, are "tinned" by being boiled in a solution containing alum, common salt, cream of tartar, and granulated tin.

204. Stannous Oxide, SnO, or Sn_2O_2, is obtained as a black powder by adding sodium carbonate to a solution of stannous chloride, and drying the precipitated hydrate in hydrogen. If the moist hydrate be boiled with a quantity of caustic potash insufficient to dissolve it, it is dehydrated and rendered crystalline. It may be obtained as a cinnabar-coloured powder by suspending the hydrate in a dilute solution of sal-ammoniac and evaporating to dryness. Stannous oxide is readily oxidised when heated; it may be ignited by contact with a red-hot body. The **hydrate** is a white amorphous powder which absorbs oxygen on exposure to air, and is readily soluble in acids and in the fixed alkalies. When boiled with certain metallic oxides, stannous hydrate acts as a reducing agent: thus it yields cuprous oxide and eventually metallic copper with a solution of a cupric salt.

205. Stannous Stannate, or Tin Sesquioxide, Sn_2O_3, is a greyish-coloured precipitate, readily soluble in ammonia, formed by boiling ferric hydrate with a solution of stannous chloride.

206. Stannic Oxide, SnO_2, occurs native as *cassiterite*, and constitutes the principal ore of the metal. It forms well-defined quadratic crystals, frequently macled (fig. 145), isomorphous with *anatase* (p. 64), generally of a dark-brown or black colour from the presence of foreign metals. It may be obtained in rhombic crystals, and of a form isomorphous with that of *brookite*, TiO_2 (p. 257), by passing stannic chloride and steam through a red-hot porcelain tube. The quadratic form of the oxide may be procured by heating amorphous stannic oxide in hydrochloric acid gas.

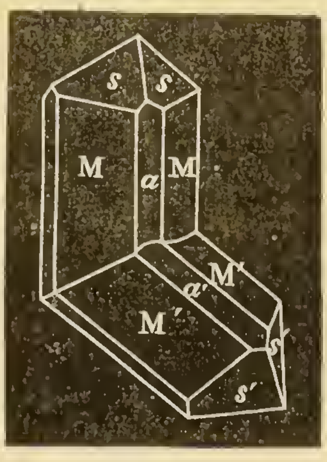


Fig. 145.

The amorphous oxide is obtained by the calcination of tin: it is a white powder which becomes transiently yellow when heated. It is used in the arts under the name of *putty-powder* for polishing glass, stone, and steel. It is also used in the manufacture of opaque glass, and in the preparation of enamels. It is not attacked by acids, but dissolves on fusion with acid potassium sulphate. On the addition of water to the solution it is precipitated. Chlorine gas converts the dioxide into stannic chloride. The *Purple of Cassius* consists of stannic oxide coloured with finely-divided gold or one of its oxides; it is not a true chemical combination, but belongs to that indefinite class of substances termed "lakes." By fusing the dioxide with a mixture of borax and microcosmic salt, quadratic pyramids isomorphous with anatase and of the composition $SnNa_2(PO_4)_2$, and rhombohedra of the composition $Sn_2Na(PO_4)_3$, are obtained. Titanium dioxide forms a compound similar in composition to the latter body. Two stannic hydrates are known, viz., **stannic acid**, H_2SnO_3, and **metastannic** acid, $H_{10}Sn_5O_{15}$. The former acid gives rise to a series of salts of the composition M_2SnO_3; the latter to a series of the formula $M_2H_8Sn_5O_{15}$.

Stannic acid is obtained as a gelatinous precipitate by the addition of hydrochloric acid to a solution of an alkaline stannate, or by adding barium or calcium carbonate to stannic chloride. On drying it forms a semi-transparent mass which reddens litmus. The most important salt of this acid is the **sodium stannate** which is used by the calico printer as a mordant. It is prepared by fusing the native dioxide with the hydrate, chloride, or nitrate of sodium; or by boiling tin-stone with solution of the hydrate: when recrystallised it has the composition $Na_2SnO_3.3H_2O$.

Metastannic acid is formed by the action of nitric acid upon tin. When dried in the air it has the composition $Sn_5O_{10}.10H_2O$: it is a white crystalline powder which dissolves slowly in solutions of the alkaline hydrates. If the solution be boiled with excess of the alkali, ordinary stannates are produced. **Sodium metastannate**, $Na_2H_8Sn_5O_{15}$, is formed when metastannic acid dissolves in a cold solution of soda. **Stannous metastannate**, $SnH_8S_5O_{15}$ (?), is a yellow powder formed by the addition of metastannic acid to stannic chloride.

207. Stannous Chloride, $SnCl_2$ or Sn_2Cl_4, is a grey translucent solid formed by heating tin in hydrochloric acid gas, or by heating "tin-salt," or hydrated stannous chloride, in closed vessels: the water is gradually expelled, and when the heat approaches redness the anhydrous chloride distils over. It melts at 250° and boils at a low red heat with partial decomposition into the tetrachloride and metallic tin.

Tin-salt, or hydrated stannous chloride, $SnCl_2.2H_2O$, is prepared for the use of the calico printer by dissolving the metal in hydrochloric acid. The salt is readily soluble in water, but its solution on exposure to air becomes turbid, owing to the formation of an insoluble oxychloride, Sn_2OCl_2.

$$3SnCl_2 + O = Sn_2OCl_2 + SnCl_4.$$

The solution forms a strong reducing agent: gold and silver salts yield the respective metals; ferric, manganic and cupric salts are converted into ferrous, manganous and cuprous compounds; indigo-blue is reduced to indigo-white, etc. The deoxidising powder of the stannous chloride is frequently taken advantage of in analytical chemistry.

208. **Stannic Chloride**, $SnCl_4$, has long been known under the name of the "fuming liquor of Libavius." It is a colourless, strongly fuming, caustic liquid of specific gravity 2·279, and boiling point 113·9°; it is prepared by the action of chlorine on tin, or by heating the metal with corrosive sublimate. It absorbs water from the air and deposits crystals of the composition $SnCl_4.3H_2O$. With one-third of its weight of water it forms the so-called *Butyrum stanni*, or *butter of tin*. This substance may also be obtained by heating stannous chloride with hydrochloric acid and a little potassium chlorate. The *nitro-muriate of tin* of commerce, the "composition" or "physic" of the dyers, is obtained by dissolving tin in cold aqua-regia, or by adding hydrochloric acid to a solution of tin crystals, together with sulphuric acid and sodium nitrate. The "pink salt" employed in calico printing is a **chlorostannate of ammonium**, $2NH_4Cl.SnCl_4$, prepared by mixing solutions of the constituent chlorides. When dilute its solution deposits stannic hydrate on boiling, which acts as a mordant by combining with any colouring matter present in the liquid.

209. **Stannous Sulphide**, SnS, is formed by heating tinfoil with sulphur. It is thus obtained as a leaden-grey crystalline powder. It may also be prepared as a black amorphous precipitate by the action of sulphuretted hydrogen

on a solution of stannous chloride. It dissolves in strong hydrochloric acid, and in yellow ammonium sulphide, forming stannic sulphide.

210. Stannic Sulphide, SnS_2, may be obtained in golden yellow spangles by passing stannic chloride and sulphuretted hydrogen through a heated tube, or by heating mixtures of finely-divided tin, sulphur, and sal-ammoniac, or of stannous sulphide and corrosive sublimate. The preparations thus obtained are known under the name of "mosaic gold." Stannic sulphide may also be prepared by passing sulphuretted hydrogen into a solution of a stannic salt: it thus forms a light-yellow powder which becomes brown on drying; it is soluble in the alkaline sulphydrates, forming salts termed *sulphostannates.*

The mineral *stannine* or *tin-pyrites*, found in Cornwall, is a mixed sulphide of copper, tin, and iron: occasionally a portion of the iron is replaced by zinc. The formula of the mineral is Cu_2MSnS_4, M being Fe or Zn.

Salts of tin readily give malleable globules of the metal when heated with charcoal in the reducing area of the Bunsen flame.

Stannous salts give a white precipitate of calomel with a solution of mercuric chloride; with auric chloride they give the "Purple of Cassius;" with stannic salts these precipitates are not formed. Sulphuretted hydrogen with stannous salts gives the dark-brown stannous sulphide; with stannic salts it produces the yellow stannic sulphide: both the sulphides are soluble in alkaline sulphides.

211. Aluminium—Symbol Al; atomic weight 27·3.—This element, as oxide and in combination with silica, is one of the main constituents of the earth's crust. Alumina was formerly regarded as identical with lime: it was shown to be distinct from that substance by Marggraff in 1754. The metal was first obtained by Wöhler in 1828 by heating the chloride with sodium, and is now prepared on a considerable scale by heating the double chloride of aluminium and sodium, $2NaCl.Al_2Cl_6$, or the native double fluoride or *cryolite*, $6NaF.Al_2F_6$, with sodium. A mixture of 10 parts of the double chloride, 5 parts of fluor-spar or cryolite, and 2 parts of sodium is thrown upon the red-hot hearth of a small reverberatory furnace, and the dampers are closed to prevent the entrance of air. Intense reaction occurs, and the materials are completely liquefied; when the reduction is finished, the slag (consisting of a mixture of common salt and aluminium fluoride) and the reduced aluminium are run out through a hole at the back of the furnace. In preparing the metal from cryolite, this mineral is mixed with half its weight of common salt, and the mixture is heated with sodium in an iron or earthen crucible. Aluminium may also be obtained by the electrolytic decomposition of the fused double chloride by a modification of the arrangement seen in fig. 5 (p. 48), or, as a deposit upon other metals, by the action of the current upon solutions of its salts. The metal obtained by reduction with sodium usually contains more or less silicon, iron, and admixed slag. Aluminium is a white, highly lustrous metal; it may be beaten out or rolled into thin foil, and drawn out into fine wire. After fusion it is somewhat soft, but by hammering it becomes as hard as the softer varieties of iron. A bar of the metal when struck emits a clear ringing sound. Its density after fusion is about 2·56, which is increased to 2·67 by hammering. It melts at a full red heat, but exhibits no tendency to volatilise. Air has no oxidising action upon it at any temperature; it is not attacked by fused nitre or by nitric or dilute sulphuric acid, sulphuretted hydrogen, or the alkaline sulphides. Hydrochloric acid and solutions of the alkaline hydroxides dissolve it readily with evolution of hydrogen; solutions of certain chlorides also act upon it slowly, with the formation of double salts. Aluminium has been found to be of considerable use in the manufacture of jewellery, in the mountings of astronomical instruments, and in the construction of balance-beams and chemical weights. Aluminium alloys readily with many metals. *Aluminium-bronze* or *aluminium-gold* contains 1 part of aluminium and 9 parts of copper: it appears to be a definite chemical compound: it is hard and malleable, has the colour of gold, and is capable of taking a high polish.

212. Alumina, Al_2O_3, the only known oxide of aluminium, is found native as *corundum* and as the gems *amethyst*, *ruby*, *sapphire*, etc., in forms derived from the hexagonal system. All the crystalline varieties of alumina are exceedingly hard: *emery*, which is mainly corundum coloured with ferric oxide, is extensively used for polishing stones, metal, etc. The oxide may be obtained artificially by adding ammonium carbonate to a boiling solution of common alum, and igniting the precipitated hydrate; or by igniting ammonia alum or aluminium sulphate to an intense white heat. The characters of the product vary with the temperature of its preparation. When produced at low temperatures it is a soft white powder of specific gravity 3·87, but after strong ignition it becomes extremely hard and acquires a density of 3·99. It fuses only at the very highest temperatures, and is insoluble in water. Amorphous alumina after ignition dissolves slowly in concentrated sulphuric and hydrochloric acids; the crystallised varieties are perfectly insoluble in all acids. Three **aluminium hydrates** are known. The **monohydrate,** $Al_2H_2O_4$ or $Al_2O_3.H_2O$, occurs native as *diaspore*. The **dihydrate,** $Al_2H_4O_5$ or $Al_2O_3.2H_2O$, is also said to occur native; it may be obtained artificially by heating a dilute solution of aluminium acetate to 100° for several days in a closed vessel: acetic acid is set free, and may be expelled by simply boiling the liquid in an open vessel; the alumina remains in solution, but may be precipitated by the addition of a few drops of any of the ordinary acids, by alkalies, and by decoctions of dye-woods. The precipitated alumina combines with colouring matters, but the character of the combination is very different from that produced by the trihydrate. On evaporating its solution, the dihydrate is obtained in the solid state; it is insoluble in the mineral acids, but dissolves in acetic acid. This soluble modification of alumina may be termed *colloidal alumina*, and is analogous to the soluble silica of Graham, obtained by dialysis (Vol. I., p. 262).

The **trihydrate,** $Al_2H_6O_6$ or $Al_2O_3.3H_2O$, occurs free as *gibbsite*, and is readily obtained artificially by adding ammonia, or its carbonate or sulphate, to a solution of ordinary alum. When dried at a gentle heat it is a soft, bulky, friable mass, which contracts greatly on ignition from loss of water. It is easily soluble in acids, and in potash and soda. By exposing the alkaline solution to the air it absorbs atmospheric carbonic acid, and the hydrate is gradually deposited in crystals: the crystalline hydrate is far less readily soluble in acids than the ordinary compound. If certain vegetable colouring matters are mixed with a solution of alum, and the alumina precipitated by the addition of an alkaline carbonate, the precipitate carries down with it the colouring matter: on account of this power to combine with colouring matters, salts of aluminium are largely used as *mordants* in dyeing and calico printing. Many of the pigments termed *lakes* are mixtures of aluminium hydrate and organic colouring matters.

By concentrating the alkaline solution of alumina, crystals of the so-called **potassium aluminate**, $Al_2K_2O_4$, are obtained. *Spinel* is a **magnesium aluminate**, Al_2MgO_4; *gahnite*, a **zinc aluminate**, Al_2ZnO_4.

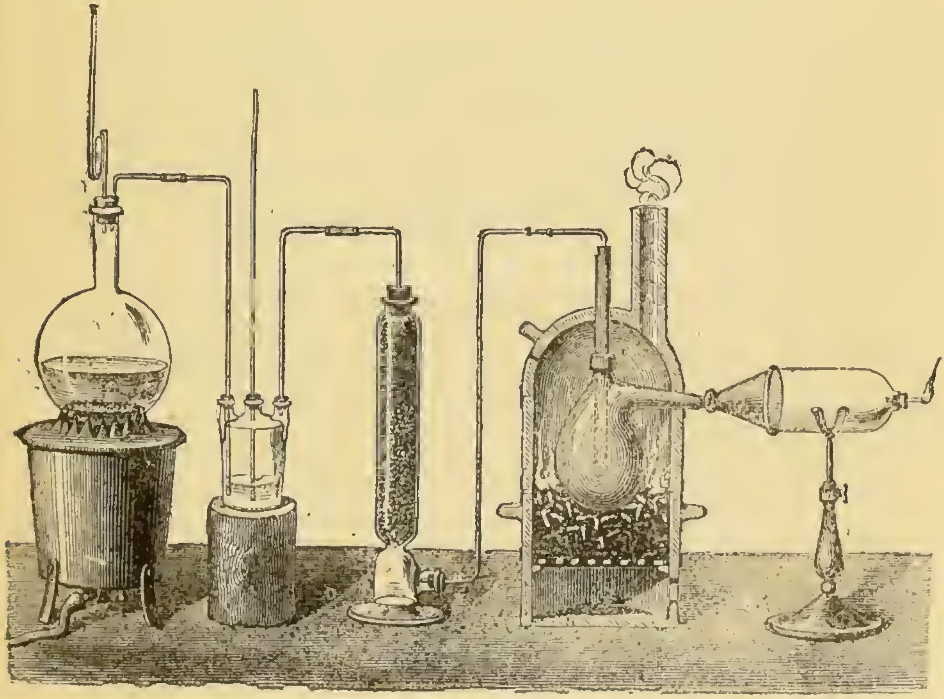


Fig. 146.

213. **Aluminium Chloride**, Al_2Cl_6, may be obtained by heating the metal in chlorine, or by igniting an intimate

mixture of alumina and charcoal, contained in a porcelain or clay retort, in a stream of chlorine gas: the aluminium chloride sublimes and may be condensed in a receiver attached to the neck of the retort. Fig. 146 represents the arrangement of the apparatus which may be employed. On the large scale, clay as free as possible from iron is mixed with pitch or tar, and the mixture is calcined and heated in an iron or earthenware cylinder through which chlorine passes, and the sublimed chloride is condensed in a chamber lined with glazed tiles.

Aluminium chloride is a fuming, highly deliquescent, colourless, waxy substance: it is readily fusible, and volatilises at about 700°. Its aqueous solution by evaporation deposits the hydrated chloride $Al_2Cl_6.12H_2O$: when heated, the crystals lose water and hydrochloric acid, and pure alumina remains. Hence the anhydrous aluminium chloride cannot be made by the evaporation of a solution of alumina in hydrochloric acid. Aluminium chloride forms double salts with a number of metallic chlorides. The most important of these salts is the **sodium aluminium chloride**, $2NaCl.Al_2Cl_6$, which is used in the manufacture of aluminium: it is prepared on the large scale by heating a mixture of alumina and sodium chloride in a stream of chlorine or hydrochloric acid. It melts at 200°, and is much less deliquescent than aluminium chloride.

214. Aluminium Bromide, Al_2Br_6, is best obtained by the direct union of its elements. It melts at 90°, and may be distilled; it is readily soluble in carbon bisulphide, and forms double salts with the alkaline bromides.

215. Aluminium Fluoride, Al_2F_6, is formed by the action of silicon fluoride on the metal. After the removal of the silicon by digestion with a mixture of nitric and hydrofluoric acids, the fluoride is obtained in small cubical crystals which are perfectly insoluble in water and in acids. A double **fluoride of aluminium and sodium**, $6NaF.Al_2F_6$, occurs native in Greenland as *cryolite*. It melts at a low red heat, and forms an opaque glass on cooling. It is used in the manufacture of aluminium and of caustic soda: to obtain the latter substance, the finely-powdered mineral is heated with lime and exhausted with water; the lime unites with the aluminium fluoride, and forms an insoluble compound, whilst the sodium hydrate remains in solution.

216. **Aluminium Sulphide**, Al_2S_3, is obtained by the action of sulphur upon aluminium heated to redness, or by passing vapour of carbon bisulphide over ignited alumina. It is decomposed by water, with formation of alumina and sulphuretted hydrogen.

217. **Aluminium Sulphates.**—The **normal sulphate**, $Al_2(SO_4)_3.18H_2O$, is found native in fibrous masses in Bohemia, Chili, Australia, etc., and constitutes the *hair-salt* or *feather-alum* of the mineralogists. It is prepared on the large scale for the use of the dyer and calico printer by treating clay with sulphuric acid. Several basic sulphates are known: a tribasic salt, $Al_2(SO_4)_3.3Al_2O_3.9H_2O$, occurs native as *aluminite*.

Aluminium sulphate forms a very important class of salts termed **alums**, of which common alum, $Al_2(NH_4)_2(SO_4)_4.24H_2O$, may be taken as the type. These salts crystallise in forms derived from the regular system: they contain 24 molecules of water, are soluble in water, and their solutions have a bitter or styptic taste and an acid reaction. **Potash alum**, one of the most important members of the series, may be obtained by adding potassium sulphate to a solution of aluminium sulphate. In the manufacture of alum on the large scale the latter salt is obtained by calcining aluminous schists containing iron pyrites. The iron sulphide is oxidised to ferrous sulphate and free sulphuric acid, which acts on the alumina to form aluminium sulphate. The aluminous schist is roasted in piles or clamps, the calcined mineral is digested with water, and the solution concentrated by evaporation. After settling, the clear liquid is drawn off and mixed with the requisite quantity of potassium chloride, the strength of the solution being so regulated that the specific gravity does not exceed 1·35. The liquor is set aside to crystallise, the crystals are washed and drained and recrystallised in casks. Potassium chloride is preferable to the sulphate, as, by its use, there is less chance of the alum being contaminated with iron; the potassium chloride is converted into sulphate by the action of the ferrous sulphate, and the highly-soluble chloride of iron is simultaneously formed. *Roman alum* is formed by calcining *alum-stone* or *alünite;* this mineral may be regarded as a basic aluminium sulphate, associated with potassium sulphate, or as a compound of dehydrated alum with the normal aluminium hydrate, $Al_2K_2(SO_4)_4.2Al_2H_6O_6$. This substance, before calcination, is insoluble in water; but, after heating, provided the temperature has not exceeded a certain point, it yields on treatment with water, alumina, and ordinary alum, which separates out on evaporation in cubical crystals.

A mixture of potash-alum and charcoal heated to redness in a covered crucible constitutes *Homberg's pyrophorus:* it consists of potassium sulphide, aluminium sulphate, and finely-divided carbon; on exposure to air it becomes red hot. Crystallised potash-alum effloresces slightly in dry air, and requires about 8 parts of water at the ordinary temperature, and $\frac{1}{3}$ of its weight of boiling water for solution. Its solution has a bitter-sweet taste, and acts readily upon iron and zinc.

Both potash and ammonia alums are largely used by dyers and calico printers as mordants: they are also used in tanning, and in medicine as astringents. **Ammonia-alum,** $Al_2(NH_4)_2.(SO_4)_4.24H_2O$, occurs native as *tschermigite,* and is prepared on the large scale by adding ammonium chloride or sulphate to a solution of aluminium sulphate. It is slightly more soluble in water than potash-alum. **Soda-alum,** $Al_2Na_2(SO_4)_424H_2O$, is also found native in certain volcanic districts: it is much more soluble in water than either of the preceding alums. **Rubidia** and **cæsia-alums** are, on the contrary, far less soluble (p. 128). **Thallium** and **silver alums** have also been prepared.

218. Aluminium Nitrate, $AlN_3O_9.9H_2O$ or $Al_2(NO_3)_6.18H_2O$, may be obtained in deliquescent prisms by concentrating a solution of aluminium hydrate in nitric acid. A mixture of this salt and acid sodium carbonate thrown into water forms a powerful freezing solution.

219. Aluminium Orthophosphate, $AlPO_4$ or $Al_2P_2O_8$, may be obtained by adding a solution of alum to sodium orthophosphate. The *Gibbsite* of Rammelsberg is a naturally-occurring hydrated aluminium orthophosphate. *Wavellite* is a basic aluminium phosphate, $2Al_2P_2O_8.Al_2(HO)_69H_2O$, occurring in rhombic crystals. *Torquois,* found in Persia, Saxony, and Silesia, has the composition $Al_2P_2O_8.Al_2(HO)_6.2H_2O$.

220. **Aluminium Silicates.**—A large number of these bodies occur native and constitute important minerals. *Kaolin* or *porcelain clay*, $Al_2O_3.2SiO_2.2H_2O$, is produced by the decomposition of orthoclase, $K_2O.Al_2O_3.6SiO_2$. *Staurolite*, which occurs in remarkably cruciform crystals (fig. 103, p. 79), has the composition $4Al_2O_33SiO_2$, a portion of the alumina being frequently replaced by ferric oxide : *andalusite* and *kyanite* have the formula $Al_2O_3.SiO_2$; *allophane* has the composition $Al_2O_3.SiO_2.6H_2O$.

Compounds of aluminium heated in the non-luminous gas flame with cobalt nitrate acquire a blue colour.

In solution the salts give no precipitate with sulphuretted hydrogen : ammonia, ammonium sulphydrate and carbonate give a white precipitate of aluminium hydrate, insoluble in excess, but readily soluble in dilute acids, even in acetic acid; caustic potash and soda afford the same precipitate, readily soluble in excess of the fixed alkali. Sodium phosphate gives a white gelatinous precipitate of the hydrated phosphate, strongly resembling aluminium hydrate: it is soluble in potash and in hydrochloric acid, but is insoluble in acetic acid.

Manufacture of Pottery.—The various clays and other aluminous minerals are largely employed in the manufacture of porcelain and earthenware. Ordinary clay when kneaded with water forms a plastic mass which is almost impervious to liquids : this fact has been known from the earliest times; vessels of clay, partially baked or hardened by exposure to the sun, were made in prehistoric ages. The principal seat of the pottery manufacture in this country is in Staffordshire, the clays which are used being mainly obtained from the South of England, principally from the counties of Devon and Dorset, and from the duchy of Cornwall. Two kinds of clay are employed by the English potter, viz., the "blue" or ball clay, and kaolin or "China" clay; for earthenware both are used, for porcelain only the last. Kaolin is a silicate of alumina, derived from the decomposition of the felspar of granite rocks; as raised from the deposits in which it occurs it is always mixed with more or less quartz, mica, and undecomposed felspar, from which it is freed by levigation, the specifically lighter kaolin being carried away in a stream of water into tanks in which it settles.

The body of earthenware is made of the "ball clay," mixed with finely-powdered flint, china clay being added in order to whiten it; a certain proportion of "Cornish stone" is also used; this substance is a product of the decomposition of felspathic rocks, and still retains sufficient alkali to render it fusible; it is added in order that by its fusion it shall bind the materials together, and so render the ware more compact, and of finer texture. These various substances always contain more or less oxide of iron which, if the quantity exceeds a certain amount, imparts an objectionable yellowish tint to the ware when fired: this colour is usually "corrected" by the addition of a small quantity of oxide of cobalt to the materials.

The following analyses express the composition of certain clays. I. is China Clay, from Cornwall. II. is a "Ball Clay," employed for common earthenware. III. is Dorsetshire Blue Clay. IV. is Common Clay, of which the ordinary red bricks are made:—

	I.	II.	III.	IV.
Silica,	46·31	66·38	46·38	49·44
Alumina,	39·91	26·08	38·04	34·26
Magnesia,	0·44	trace	trace	1·94
Lime,	0·43	0·84	1·20	1·48
Ferrous oxide,	0·27	1·26	1·04	7·74
Water,	12·67	5·14	13·57	5·14
	100·03	99·70	100·23	100·00

The ingredients are first carefully reduced to fine powder, and are intimately mixed and suspended in water, so as to form a thin paste, technically known as "slip." To dry it, the slip is either passed over the surface of brick kilns, or the greater portion of the water is squeezed out by filtration under pressure. The plastic mixture is then fashioned into the various shapes which are required, either by means of the potter's wheel, or by pressing, moulding, and turning. The ware is next dried, and placed in vessels made of fire-clay, known as "saggers," which are arranged one above the other in columns, in a cylindrical oven, surmounted by a dome, the flues in which are so constructed that the various portions can be gradually and uniformly heated. The baked ware is now known as *biscuit:* if it is required to be decorated, the figures are next imprinted on it. The pattern is first printed with metallic colours, mixed with oil, on tissue paper, specially made for the purpose. The print is laid evenly upon the biscuit, and the back rubbed with a pad of flannel, when the colours transfer themselves to the ware, and after dipping the article into water, the paper is readily detached. The printed ware is again heated to redness, to burn away the oil, and to *harden-on* the colour. It is next *glazed*, in order to render it impervious to liquids. The glaze is usually composed of materials similar to those which constitute the main body of the ware, mixed, however, with some substances to render them fusible. A considerable amount of judgment is needed in the preparation of the glaze. It must not be too easily fused, otherwise it will eventually become dull; and it must be perfectly transparent, so that the pattern on the ware may be distinct, and the colours, if possible, made more brilliant; and lastly, it must expand and contract under the influence of heat or cold *pari passu* with the body of the ware, otherwise it will crack. Formerly, the glazing was effected by coating the articles with finely-powdered galena or lead sulphide; on firing, this was converted into a readily-fusible and transparent lead silicate. The fluxes now employed are generally oxides and carbonates of lead, potash, soda, or lime, borax, and barium sulphate. If the materials used for the glaze are insoluble in water, they are simply finely powdered and suspended in that liquid, and the biscuit-ware is dipped into the "slip;" the water rapidly percolates the porous material, leaving the finely-divided powder adhering to the surface. If soluble salts enter into the composition, the materials are first melted together in crucibles, and the insoluble glass or *frit* is finely powdered and suspended in water, as in the preceding case. The ware after dipping is again fired, when the glaze melts and spreads evenly over the surface. The glazing of the commonest kinds of earthenware is effected by throwing common salt upon the heated ware; a dark-coloured fusible silicate of sodium and iron, insoluble in water, is thus formed upon the surface.

The composition of earthenware is very variable: Analysis I. may however be taken to represent the average proportion of its constituents; analysis II. shows the composition of a glazing mixture—

	I.		II.
Silica,	68·55	Silica,	43·66
Alumina and oxide of iron,	29·13	Lime,	0·52
Lime,	1·24	Alumina,	9·56
		Borax,	20·08
		Chalk,	10·08
	98·92	Lead carbonate,	15·19
			99·09

Occasionally, as in the manufacture of tiles and of majolica, the surface of the ware is covered with a richly-coloured glass, made opaque by the use of oxide of tin. Palissy ware is similar to majolica, except that the coloured glazes are transparent. Plain tiles are made by compressing dry clay, reduced to powder, into moulds, by means of hydraulic pressure; in encaustic tiles the patterns are sunk below the surface, and the spaces are filled with differently-coloured "slips."

Earthenware is distinguished from porcelain by the peculiarities of its fracture: in earthenware it is earthy and porous, and shows very little trace of fusion; moreover, the glaze is perfectly distinct from the body of the ware, and may frequently be detached with more or less ease. Porcelain breaks with a conchoidal fracture: it is semi-vitreous and translucent, and no line of demarcation can be traced between the glaze and the body of the ware. Porcelain may, in fact, be regarded as intermediate in character between true earthenware and glass. It is essentially composed of kaolin and felspar, occasionally mixed with alkaline or alkaline-earthy silicates. At the high temperature of the porcelain furnace the felspar and lime and alkaline silicates are fused, and partially combine with the kaolin or aluminium silicate to form a compact and homogeneous product. The manufacture of porcelain originated with the Chinese, who, six or seven hundred years ago, produced ware of a degree of perfection which European porcelain has barely attained to even now. Several of the sixteenth century alchemists made efforts to discover the secret of the manufacture; and it is probable that from the results of their trials Francis de Medici was able to produce those pieces with which his name is associated. English porcelain differs from that of the Chinese, or the modern French and German, which varieties are made entirely from kaolin and felspar, by containing a considerable amount of calcium phosphate, or ground bone-ash. After firing it is glazed by immersion in a "slip" of felspar and ground quartz or flints. For some varieties glazes of silicates or borates of lead are employed.

The translucency of statuary or Parian porcelain is obtained by the regulated addition of the fusible Cornish stone or felspar: the cream colour or tint of the English variety, which contrasts so favourably with the bluish-white colour of the Continental productions, is due to a minute portion of ferric oxide contained in the clay, the colouring effect of which is produced by careful firing.

The following analyses show the composition of several varieties of porcelain: I. is a Chinese porcelain of specific gravity 2·314; II. is Berlin porcelain of which the evaporating dishes of the chemist are composed; III. is an English porcelain—

	I.	II.	III.
Silica, ...	71·04	72·96	39·38
Alumina, ...	22·46	24·78	21·48
Lime,......................	3·82	1·04	10·06
Bone-earth, ...	...	..	26·44
Alkalies, ...	2·68	1·22	2·14
	100·00	100·00	100·00

Manufacture of Glass.—Glass, as ordinarily made, is a mixture of various insoluble silicates with excess of silica; *crown, sheet,* and *plate glass* contain double silicates of lime, potash, or soda; *flint-glass* is a double silicate of lead and potash.

Common window-glass is made by fusing together a mixture of white sand, salt-cake or sodium sulphate, lime, and a little charcoal or coal in a large crucible or pot made of well-baked

Stourbridge clay. The proportions vary considerably, but the following is stated to be a good mixture:—

Sand,	20	parts.
Salt-cake,	10	,,
Quick-lime,	5	,,
Charcoal or Coal,	1	,,

The minerals are powdered, mixed, and heated for some time, in order to dry them thoroughly: the sintered mass or "frit," as it is technically termed, is then thrown into the heated glass-pots, in which it melts. The "founding" or thorough melting of the mixture requires about sixteen hours. Before the glass can be worked it is necessary to remove the scum of uncombined sodium sulphate, known as *sandiver* or *glass-gall*, from the surface; the addition of "cullet" or broken glass facilitates its separation. When the fluid mass is perfectly clear and free from bubbles of gas, the temperature of the furnace in which the pots are placed is reduced until the glass becomes pasty. The reaction which takes place in the pots is very simple. At the high temperature the sulphuric acid of the salt cake is expelled by the silica, and sodium silicate is produced: at the same time the lime combines with silica, either by direct action or through the intervention of the alkaline silicate, and eventually a double silicate of lime and soda is obtained, in which the excess of the silica dissolves. The charcoal or coal assists in the expulsion of the sulphur, and prevents the peroxidation of the iron. To fashion the glass into sheets, the blower inserts the end of his blowpipe, an iron tube of about five feet in length, into the molten mass, and when he has collected a sufficient quantity of the "metal," as the unworked glass is technically termed, he removes the pipe from the pot and blows into the other end so as to distend the mass into a globular or pear-shaped form. By swinging the blowpipe like a pendulum, the pear-shaped vessel is gradually elongated into a cylinder with rounded ends. The workman then closes the mouth of the pipe with his thumb, and places the extreme end of the glass cylinder into the mouth of the furnace: it is thus softened, and is burst by the expanding force of the enclosed air. The opening thus made is rapidly widened by a tool until it is of the same diameter as the cylinder; by drawing a thread of molten glass round the end attached to the blowpipe, and touching it with a cold iron tool, the cylinder cracks, and can be separated from the iron tube. The detached cylinder is slowly cooled, and is cut longitudinally by a diamond. It is next placed on the hot, smooth floor of the "flattening-kiln," with the slit uppermost; at the high temperature of the furnace the glass softens, so that it can be unrolled, as it were, by the workman widening the cut by means of a wooden tool, and pressing out the curved surface on either side until the glass is flattened against the floor of the kiln. The sheet or table is then removed to the "annealing oven," in which it is slowly cooled.

Dome-shaped glass shades are made in a similar manner to the cylinders: if they are required of oval or square base, they are blown within wooden moulds, the inner sides of which are charred.

In making *crown-glass* the mass of melted glass on the end of the blowpipe is fashioned into a globular form as in making sheet-glass. A pointed iron rod, known as a *puntil* or *pointel*, armed at the end with a small quantity of soft glass, is affixed to the under surface of the globe, and by touching the shoulder with a cold iron tool the globe is detached from the blowpipe. The blower places the globe on the pointel which serves as a handle, in the mouth of the furnace: the glass is gradually softened by the heat, and by rapidly rotating the pointel the opening in the globe at the point where the blowpipe was attached is gradually widened until the glass suddenly assumes the form of a circular sheet; this is detached from the pointel and sent to the annealing furnace.

In the manufacture of *plate-glass* the melting-pot is lifted from the furnace by a crane, and the pasty "metal" is poured upon an iron table, and is spread out by the action of a roller travelling backwards and forwards over its surface. After having been annealed, the plate is embedded in plaster of Paris, and a precisely similar plate, fixed to suitable machinery, is caused to rotate over it, fine sand suspended in water being thrown between the plates: the surfaces of the two plates are thus ground by their mutual friction; after a time the sides are reversed and are ground one against the other in exactly the same way. The roughened surfaces, which now resemble that of ground glass, are then polished by emery and oxide of iron until they are perfectly smooth.

Flint-glass, of which tumblers, wine-glasses, etc., are made, is prepared by fusing a mixture of red lead, fine white sand, and pearl ash, with the addition of a small quantity of manganese dioxide. Manganese compounds impart to glass an amethystine or purple tint which is complementary to the light-green colour which, in the absence of the manganese, would be produced by the oxide of iron present in the materials. Since a mixture of two complementary colours produces white light, the decolourising action of the manganese may be considered to be rather an optical effect than due to any chemical action between the two oxides. The mixture employed in the manufacture of the best flint-glass may be represented as follows:—

White sand,...........................	6	parts.
Red lead,..............................	4	,,
Pearl ash,.............................	3	,,

although these proportions are frequently varied.

Flint-glass is much denser, has a higher refractive power, and hence is more brilliant than crown or sheet glass: it fuses at a lower temperature, and is more readily worked than the lime glasses; on the other hand, it is much softer, and is therefore more easily scratched than these glasses; it is also more readily acted upon by acid and alkaline solutions.

The brown or black glass used for making bottles of common quality is made from ordinary sand, lime, and salt-cake, the materials being fused together on the bed of a reverberatory furnace, and the molten glass cast into moulds of the required form. Its dark colour is due to the large proportion of oxide of iron present in the sand.

The hard infusible Bohemian glass used for making the combustion-tubing of the chemist contains, on the average, about 75 per cent. of silica, 15 of potash, and 10 of lime.

Various colours are imparted to glass by the addition of certain metallic oxides. Thus oxide of manganese gives a violet colour; ferrous oxide, a light-green colour; ferric oxide, a light-brown; cuprous oxide, a blood-red; cupric oxide, a greenish-blue; gold, a ruby colour; oxide of chromium, a bright-green; oxide of uranium, a greenish-yellow. The brownish-red colour of *aventurine* glass is due to the dissemination throughout it of finely-divided metallic copper. *Enamels* are glasses made opaque by the addition of the oxides of antimony, arsenic, or tin, or by excess of bone-ash.

The following analyses serve to show the composition of the chief varieties of glass :—

	Window-Glass.	Crown-Glass.	Flint-Glass.
Silica, ...	69·0	67·7	56·0
Lime, ...	12·5	9·9	...
Alumina, ...	7·4	1·4	1·0
Soda, ...	11·1	...	...
Potash, ...	...	21·0	8·6
Lead oxide, ...	...	...	34·4
	100·0	100·0	100.0

Glass, when heated, expands in a remarkably fitful or irregular manner, as if its particles were in a state of continual tension and required the expenditure of considerable force to make them assume positions of stable equilibrium : on cooling, similar irregularities in the contraction are observed ; hence a glass vessel on cooling does not at once acquire its normal capacity corresponding to the temperature which it possesses when cold. This phenomenon is frequently observed in the case of thermometers which have been heated to high temperatures and allowed to cool suddenly : after such treatment their zero points are invariably below the original position, owing to the enlargement of the bulb. After a time, however, the bulb assumes its ordinary size.

By heating and sudden cooling, glass becomes exceedingly brittle and readily flies to pieces when scratched, or when attempts are made to break off a portion. The well-known Rupert drop is a pear-shaped piece of glass obtained by pouring molten glass into water : on snipping off the pointed end of the drop the mass flies to pieces from the sudden disturbance of the tension between the particles due to the rapid cooling. By allowing the heated glass to fall into hot oil it becomes much harder and less easily broken than ordinary glass ; the so-called *toughened* or *tempered glass* is made in this manner : the state of such glass is very similar to that of the Rupert drop; when fractured it flies to coarse powder. In manufacturing articles of ordinary glass it is necessary to cool them very slowly, otherwise they are as liable to fracture as the Rupert drop; accordingly, as soon as they are blown or cast, they are placed in the "annealing oven," in which their temperature is very slowly reduced.

Many varieties of glass, especially those containing relatively large quantities of silicates of lime and alumina, when heated for some time in the furnace, become opaque, and are converted into a substance resembling porcelain. This change was first observed by Reaumur; its cause is not exactly known: it appears, however, to be accompanied by a loss of alkali and by the separation of silicates in a more or less crystalline condition.

Glass is very slowly acted upon by water under ordinary circumstances, but if it be finely divided and the water heated, appreciable quantities of the alkali are dissolved out: the pearly surface of antique glass is due to a thin coating of free silica, the alkali having been extracted by the action of moist air or earth. Most varieties of glass are acted upon to some extent by acids and alkalies: potash and soda extract the silica, and hot solutions, containing free phosphoric, nitric, and sulphuric acids, dissolve out the bases: these facts are too frequently lost sight of in analytical work. Hydrofluoric acid, both as gas and in solution, rapidly attacks glass with the formation of silicon fluoride, and of the double fluorides of silicon, calcium, and the alkalies.

Ultramarine.—Certain minerals, as, for example, *hauyne* and *nosean*, are occasionally met with containing a blue colouring matter, consisting apparently of silica, alumina, soda, and sulphur. This colouring matter seems to be identical with that of *lapis-lazuli*, a rare mineral occurring associated with iron-pyrites, in certain limestone districts in China, Thibet, and various parts of South America, and highly esteemed on account of its rich blue colour. Lapis-lazuli is not a definite chemical compound, but is a decomposition-product formed in all probability by the action of sulphur upon a double silicate of alumina and soda, *e.g.*, soda-felspar. Its colouring matter, known as *ultramarine*, was formerly extracted from it by a tedious and empirical series of operations.

The observation that a blue colouring matter, analogous to that of lapis-lazuli, frequently occurs in soda-ash and lime furnaces, led to the idea that ultramarine might be artificially prepared, and in 1828 Christian Gmelin discovered a mode of making this substance which is substantially identical with that now employed, and by which ultramarine may be obtained of even a finer colour than that of the natural variety. A mixture of kaolin, charcoal, and sodium sulphate or carbonate is heated to redness in closed fire-clay crucibles, and the green mass thus formed is ground to powder and roasted in thin layers with flowers of sulphur, until the required blue shade is obtained. The following analyses will serve to give an idea of the composition of the different products—

	Green.	Blue.
Silica,	38·494	41·058
Alumina,	22·152	26·078
Soda,	14·135	13·597
Potash,	0·506	...
Sulphuric acid,	0·731	1·250
Sulphurous acid,	0·427	0·883
Thiosulphuric acid,	...	0·703
Sodium sulphide,	9·063	7·452
Free sulphur,	3·491	8·977
	99·999	99·998

The true nature of ultramarine is not known: it has been variously regarded (1) as a compound of aluminium silicate with sodium sulphide and sulphate; (2) as a double silicate of aluminium and sodium in combination with sodium sulphide; and (3) as a double silicate of aluminium and sodium in which the oxygen has been partly replaced by sulphur.

When heated with hydrochloric acid, ultramarine evolves sulphuretted hydrogen and is decolorised: at a high temperature, also, it loses its colour.

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221. Zirconium—Symbol Zr; atomic weight 89·6.—This rare element was discovered by Klaproth in 1789, in the mineral *zircon* or *jargon*, SiO_2ZrO_2. Zirconium may be obtained as an amorphous powder by heating potassium zirconium fluoride with potassium; or in crystals by heating this compound with aluminium. The crystalline variety resembles antimony in many of its physical properties. Its specific gravity is 4·15. It is unalterable when heated in the air, but ignites when heated in chlorine, forming the tetrachloride.

222. Zirconia, ZrO_2, is obtained from zircon by fusing it with caustic soda in a silver crucible. The fused mass is treated with hydrochloric acid, evaporated to dryness, to render the silica insoluble, digested with water, and the zirconia precipitated as hydrate by adding ammonia to the filtered solution. As thus prepared it is a white, tasteless powder, which, on heating parts with its water of hydration, becomes incandescent: by fusion with borax, and exhaustion with hydrochloric acid, it is obtained in crystals isomorphous with those of *rutile* and *cassiterite.*

223. Zirconia Hydrate is obtained by adding ammonia to a solution of a zirconium salt; it forms a white gelatinous mass resembling recently-precipitated silica: on drying, it shrinks to a translucent, gummy mass, possessing a conchoidal fracture. It is slightly soluble in water, and its solution reddens litmus and turmeric paper.

Zirconia, like silica, combines with basic oxides to form salts termed **Zirconates.**

224. Zirconium Chloride, $ZrCl_4$, may be obtained by heating the metal in chlorine gas, or by igniting a mixture of zirconia and charcoal in chlorine. It resembles aluminium chloride in its physical properties. Its aqueous solution deposits the hydrated salt in colourless silky needles, which evolve hydrochloric acid on heating, and give an oxychloride of the composition $ZrOCl_2.9H_2O$. Zirconium chloride combines with phosphorus pentachloride to form the compound $2ZrCl_4.PCl_5$. A double chloride of zirconium and sodium is also known of the formula $ZrCl_4.2NaCl$.

225. Zirconium Fluoride, ZrF_4, is best formed by heating zirconia with ammonium hydrogen fluoride. It is readily soluble in water, and on evaporation from solutions containing free hydrofluoric acid, yields the hydrated fluoride $ZrF_4.3H_2O$, in triclinic crystals. Zirconium fluoride combines with certain metallic fluorides to form salts, termed **fluozir-**

conates, many of which may be obtained in well-defined crystals, isomorphous with the corresponding fluosilicates and fluostannates.

226. **Zirconium Sulphide** is a dark-brown powder, formed by the direct union of its elements: its composition is unknown.

Zirconium resembles cerium and thorium in many of its reactions: it is however distinguished from these metals by affording a precipitate of the thiosulphate when heated with solution of sodium thiosulphate. Zirconium in solution may also be distinguished by the formation of a precipitate of basic potassio-zirconic sulphate on the addition of a hot solution of potassium sulphate.

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227. **Cerium**—Symbol Ce; atomic weight 138.—This element was discovered independently by Klaproth and by Hisinger and Berzelius in 1803, in a hydrated cerium silicate, termed *cerite*. Cerium has the colour and lustre of iron, and is capable of taking a high polish: it is unacted upon by dry air, but is slightly corroded by moist air. It is malleable, and may be drawn out into wire of great flexibility. It burns in the air at a much lower temperature than magnesium, and with greater brilliancy: showers of sparks are produced when a mass of the metal is struck with a flint. Cerium burns in chlorine, and combines directly with iodine, sulphur, and phosphorus. It is scarcely acted upon by the concentrated mineral acids, but when they are diluted they readily dissolve it.

Cerium combines with oxygen in two proportions to form a sesquioxide, Ce_2O_3, and a dioxide, CeO_2.

The **sesquioxide** is a greyish-blue powder which rapidly oxidises on exposure to air: it is formed by heating the oxalate in hydrogen.

The **dioxide** is formed when the oxalate, carbonate, or nitrate is heated in the air. It has a light-yellow colour, changing temporarily to a deep-orange on heating. It may be obtained in crystals belonging to the regular system by heating cerous chloride with borax, and treating the fused mass with hydrochloric acid.

228. **Cerous Chloride**, Ce_2Cl_6, is a white, porous fusible mass, obtained by heating the sulphide in chlorine, or igniting the cerous ammonium chloride in chlorine. Its solution absorbs oxygen from the air, and forms double salts with platinum tetrachloride and auric chloride, isomorphous with the corresponding salts of lanthanum.

Ceric Chloride, $CeCl_4$, is obtained by dissolving the dioxide in hydrochloric acid.

229. **Cerous Sulphate**, $Ce_2(SO_4)_3.9H_2O$, is obtained in hexagonal prisms by evaporating a solution of cerous oxide or carbonate in sulphuric acid at a temperature of about 50°. By evaporation in a vacuum at ordinary temperatures the salt crystallises in octahedrons with 8 molecules of water: it is isomorphous with the corresponding lanthanum sulphate, but not with the didymium salt.

A number of **ceric sulphates** are obtained by dissolving the dioxide in sulphuric acid.

Cerium compounds, when heated with borax in the outer flame, give a glass which is deep-red whilst hot, but becomes colourless on cooling. With solutions, ammonium sulphide gives a precipitate of the hydrated sesquioxide; caustic potash gives the same precipitate, insoluble in excess of the precipitant. Potassium sulphate gives a sparingly soluble double salt. Ammonium oxalate produces cerous oxalate, which on heating in the air forms the dioxide of a yellow colour when cold, but changing to orange-red on heating.

230. **Lanthanum**—Symbol La; atomic weight 139 (Cleve).—This rare element was discovered by Mosander, in 1839, in the mineral *cerite*. The metal resembles cerium; it is, however, oxidised more rapidly on exposure to air, and is attacked by strong nitric acid in the cold; it is neither so ductile nor so malleable as cerium, and requires a much higher temperature for ignition. The **oxide**, La_2O_3, is a heavy white powder, obtained by igniting the carbonate or oxalate; it slakes in contact with water, forming the **hydrate**, LaH_3O_3, a soft white powder, resembling lime both in its appearance and in its property of rapidly absorbing carbonic

acid. The **chloride** is a highly soluble salt: when crystallised from its solution over strong sulphuric acid it has the composition $La_2Cl_6.12H_2O$. On heating this substance in air it forms an **oxychloride.** The **sulphide,** La_2S_3, is a bright yellow crystalline powder, obtained by heating the oxide in the vapour of carbon disulphide. The **sulphate,** $La_2(SO_4)_3.9H_2O$, forms small prismatic crystals, which are more soluble in cold than in hot water. It forms sparingly soluble double salts with the alkaline sulphates, similar to those formed by cerous sulphate.

Salts of lanthanum in solution give a gelatinous precipitate of the hydrate on the addition of caustic potash, insoluble in excess, but soluble in chlorine water. Ammonium oxalate produces a white flocculent precipitate.

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231. Titanium—Symbol Ti; atomic weight 50.—This element was discovered in 1791 by Gregor, in the titaniferous iron-sand of Cornwall. The metal itself is never found native. Its principal naturally-occurring compounds are the minerals *rutile, brookite,* and *anatase,* which consist of the dioxide TiO_2; the titaniferous iron ores; calcium titanate; and *sphene* or *titanite,* a calcium silico-titanate. The rare minerals *æschynite, polycrase,* and *pyrochlore,* are compounds of titanic oxide, zirconia, ceric, lanthanic, niobic oxides, yttria, etc. Small quantities of titanic oxides are found in many clays and iron ores. The bright copper-coloured cubical crystals occasionally found in iron slags are composed of a **cyanonitride of titanium,** $TiCy_2.3N_2Ti_3$. These crystals may be obtained by passing nitrogen over a strongly heated mixture of titanic oxide and charcoal. Titanium, indeed, manifests a remarkable affinity for nitrogen, several nitrides being known.

Titanium is obtained as a dense amorphous powder by heating potassium-titanium-fluoride with potassium; or in crystals by passing the vapour of the tetrachloride over heated sodium. The finely-divided metal readily ignites when heated in the air, and burns with great brilliancy. When ignited in chlorine it forms the tetrachloride; when heated with water hydrogen is evolved; in presence of hydrochloric aid the evolution of the gas is very rapid.

Titanium unites with oxygen to form two well-defined compounds, viz., **titanous oxide**, Ti_2O_3, and **titanic oxide**, TiO_2. A monoxide, TiO, is supposed to exist, but it has not yet been satisfactorily isolated.

Titanium sesquioxide, or titanous oxide, Ti_2O_3, is obtained as a black powder by heating the dioxide in hydrogen. It dissolves in acids, forming violet solutions, which act powerfully as reducing agents. On the addition of an alkali they give a brown precipitate of titanous hydrate, which gradually becomes blue, and then white, by combination with oxygen to form the dioxide.

Titanium dioxide, or titanic oxide, TiO_2, is found native, principally as *rutile*. When pure it forms a reddish-brown powder. It may be obtained in crystals, identical with those of rutile, by passing the vapour of the tetrachloride and steam through a red-hot tube, or by strongly heating the amorphous oxide in hydrochloric acid or hydrofluoric acid gas. It is stated that three forms of the crystallised oxide may be thus obtained: anatase being formed at a low red heat, brookite at a higher temperature, and rutile at a white heat. Titanium dioxide, after strong ignition, is insoluble in all alkalies and acids, except strong sulphuric and hydrofluoric acids. By fusion with acid potassium sulphate, it yields a yellow liquid, which on cooling dissolves in water forming a clear solution.

232. Titanic Hydrate, TiH_4O_4, is formed by decomposing the tetrachloride with water. It is a white powder, which on heating to 120° gives up a portion of its water and is converted into TiH_2O_3. At still higher temperatures other hydrates containing less water are obtained. These compounds dissolve readily in dilute mineral acids, but the solutions, when boiled, deposit **metatitanic hydrate** as a white powder, insoluble in all acids with the exception of oil of vitriol. A dilute solution of titanic hydrate in hydrochloric acid, when subjected to dialysis, yields colloidal titanic acid, analogous to soluble silicic acid (see Vol. I., p. 262).

Titanic hydrate combines with both acids and bases. The acid compounds are exceedingly unstable, and have been but little investigated. The salts of titanic acid may be classed under the general formulæ M_4TiO_4 and M_2TiO_3, corresponding to the ortho- and meta- silicates. The best known titanates are calcium titanate, $CaTiO_3$; *sphene*, $CaSiO_3.CaTiO_3$; and *ilmenite* or *menaccanite*, $FeTiO_3$.

233. **Titanium Trichloride**, Ti_2Cl_6, is obtained in the form of dark-violet lustrous scales, by passing the tetrachloride, mixed with hydrogen, through a heated tube, or by heating the tetrachloride with metallic silver in a sealed tube. It is extremely deliquescent, and dissolves in water, forming a reddish-violet solution, which gives a precipitate of brown titanous hydrate on addition of alkalies or ammonium sulphide. The same solution may be obtained by digesting finely-divided silver with a solution of titanic acid in hydrochloric acid.

234. **Titanium Tetrachloride**, $TiCl_4$, is obtained as a colourless, fuming, volatile liquid by heating titanium or its nitride in chlorine, or by passing chlorine over a heated mixture of titanic oxide and charcoal. It boils at 136·14° under a pressure of 752·3 mm., and has a specific gravity of 1·7606 at 0° It becomes turbid on exposure to moist air, and gradually solidifies, owing to absorption of water, forming an **oxychloride** of the composition $TiCl_4.3TiO_2.16H_2O$. On adding water to the tetrachloride a considerable rise of temperature is produced, and a solution of the hydrate in hydrochloric acid is formed, from which metatitanic acid is precipitated on boiling. The tetrachloride rapidly absorbs ammonia, forming a yellowish powder, $4NH_3.TiCl_4$, which, by ignition in ammonia gas, is converted into the nitride, $3TiN_2.Ti_2N_2$. The tetrachloride combines directly with hydrocyanic acid to form lemon-yellow crystals of the composition $TiCl_4.HCy$; with nitrogen tetroxide it forms a yellow crystalline compound, $3TiCl_4.2NOCl$; with anhydrous ether it forms $TiCl_4.C_4H_{10}O$, an amber-coloured crystalline mass, melting between 42° and 45°, and titanium ethyltrichlorhydrin $TiCl_3.C_2H_5O$, a pale yellow crystalline body, melting at about 76°, and boiling at about 187°. With phosphorus pentachloride it forms titano-phosphoric chloride, $TiCl_4.PCl_5$, a light-yellow crystalline mass, soluble without decomposition in ether, very hygroscopic, and decomposed by water. Phosphoryl trichloride and sulphur tetrachloride also

form unstable combinations by direct union with titanium tetrachloride.

235. **Titanium Tetrabromide**, $TiBr_4$, is an amber-coloured crystalline mass of specific gravity 2·6, melting at 39° and boiling at 230°. It is prepared by processes analogous to those which yield the tetrachloride, and behaves with reagents in a manner similar to that compound.

236. **Titanium Iodide**, TiI_4, may be formed by passing hydriodic acid gas into the gently heated tetrachloride. It is a brittle, crystalline, lustrous mass, of a reddish-brown colour, melting at 150°, and boiling above 360° without decomposition.

237. **Titanium Trifluoride**, Ti_2F_6, is a violet powder formed by igniting potassio-titanic fluoride in hydrogen.

238. **Titanium Tetrafluoride**, TiF_4, is a fuming colourless liquid, formed by heating a mixture of titanic oxide, fluorspar, and oil of vitriol in a platinum retort. By dissolving titanic oxide in hydrofluoric acid crystals of **hydrotitanic fluoride**, H_2TiF_6, are obtained. By replacing the hydrogen in this compound, by metallic radicles, a series of well-defined and stable salts may be obtained.

239. **Titanium Disulphide**, TiS_2, is formed by passing vapour of carbon disulphide over the strongly-heated dioxide. It forms large, brass-yellow, lustrous crystals.

Titanium compounds, heated with microcosmic salt in the inner flame, give a glass, yellow whilst hot, violet when cold. Solutions of the salts in hydrochloric acid, or, better, sulphuric acid, give a precipitate of the dioxide on boiling. On adding metallic tin to the solution a dark violet-blue precipitate is formed, which gradually becomes white from absorption of oxygen.

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240. **Cobalt**—Symbol Co; atomic weight 58·7.—Compounds of cobalt appear to have been known to the ancients and used by them in colouring glass. The metal itself was first isolated by Brand in 1733. Metallic cobalt is occasionally found in meteoric iron associated with nickel and phosphorus. Its principal naturally-occurring compounds are the arsenide,

smaltine or *tin-white cobalt* ($CoAs_2$): *cobalt bloom* or *erythrine*, a hydrated arsenate, $Co_3As_2O_8.8H_2O$, and *cobalt glance*, a sulpharsenate, Co_2AsS. The metal is best obtained by igniting the oxalate in a covered crucible: at a high temperature it may be obtained as a fused regulus of a grey colour, exceedingly hard, highly malleable and ductile, and capable of taking a polish; its specific gravity is about 8·9. It is unalterable in air even when moist, but at a high temperature it takes fire, forming a cobaltoso-cobaltic oxide. It dissolves slowly in acids with evolution of hydrogen, forming red solutions. It is slightly magnetic, and preserves this property even when alloyed with mercury.

Cobalt unites with oxygen to form **cobaltous oxide**, CoO, and **cobaltic oxide**, Co_2O_3.

The protoxide is used for the production of a beautiful blue colour on porcelain. *Zaffre* is an impure cobalt oxide prepared by roasting cobalt ores mixed with sand. *Smalt* is prepared by fusing partially-roasted cobalt ores with a mixture of powdered quartz and pearl-ash. A silicate of potash is thus formed in which the cobalt oxide dissolves with the formation of a bright-blue colour. The mass whilst still hot is thrown into water and is ground to powder under granite stones. Smalt is principally used by paper stainers, and to some extent as a pigment. *Thénard's blue* is produced by heating alumina with cobalt oxide. It is made by adding potassium phosphate to a solution of cobalt nitrate: the precipitate thus obtained is mixed with alumina, dried and heated in covered crucibles. *Rinman's green* has a similar composition, zinc oxide being substituted for alumina. *Cobalt yellow* is a compound of cobalt oxide, potash, and nitrogen tetroxide, formed by adding an alkaline solution of potassium nitrite to an acid solution of cobalt nitrate. The formation of this precipitate is occasionally used as a test for cobalt. Its composition varies with the manner of preparation: its usual composition is $Co_2K_6(NO_2)_{12}$ or $Co_2O_3.3N_2O_3 + 3(K_2O.N_2O_3) + xH_2O$.

Several intermediate oxides are known, viz., Co_3O_4 or $CoO.Co_2O_3$, Co_6O_7 or $4CoO.Co_2O_3$, and Co_8O_9 or $6CoO.Co_2O_3$.

Cobaltous oxide, CoO, is obtained by igniting the hydrate or carbonate out of contact with air. It is a greenish-grey powder, readily reduced to the metallic state by ignition in hydrogen, and is converted into the sesquioxide in presence of oxygen. The hydrate, CoH_2O_2, is obtained by adding potash to a solution of a cobaltous salt. A blue basic salt is first formed which gradually changes to a rose-coloured hydrate. The hydrate readily loses water at 100°: on exposure to air it absorbs oxygen.

The sesquioxide, Co_2O_3, is formed by adding a hypochlorite to a solution of a cobalt salt, or by passing chlorine into water containing the protoxide in suspension. It is a black powder which, when ignited, yields Co_3O_4, corresponding to the magnetic oxide of iron. This oxide is also used as a pigment in enamel painting.

241. **Cobaltous Chloride**, $CoCl_2$, is obtained in blue crystalline scales by heating the metal in chlorine, or by adding strong hydrochloric acid to a solution of the protoxide in hydrochloric acid. When dilute, the solution has a pink colour, but by rapid evaporation it turns blue. If the dried mass be strongly heated, the anhydrous chloride sublimes: it possesses a light-blue colour, and is extremely deliquescent: by absorption of water its colour changes to red. By the cautious evaporation of the pink solution, red crystals of the hydrated chloride may be obtained of the composition $CoCl_2.6H_2O$.

Cobaltic Chloride, Co_2Cl_6, appears to be formed by dissolving the cobaltic oxide in cold hydrochloric acid. It cannot be isolated; on warming its solution chlorine is evolved and the protochloride is formed.

242. **Cobaltous Bromide, Iodide,** and **Fluoride**, have a similar constitution to the chloride, and behave like that salt on hydration. The iodide is especially remarkable from the variations of its colour when combining with water. When anhydrous it is black and of a graphitic lustre, but as it takes up moisture from the air it gradually acquires a bright moss-green tint corresponding to the composition $CoI_2.2H_2O$, and ultimately becomes pink from the formation of the hexhydrated salt $CoI_2.6H_2O$. (Hartley.)

243. **Cobalt Sulphide**, CoS, forms the mineral known as *syepoorite:* it is found in North-West India, and is said to be employed by the Indian jewellers to give a red colour to

gold. It may be formed artificially by heating the metal or its oxides with sulphur. It is obtained hydrated and of a black colour by adding a solution of an alkaline sulphide to a cobalt salt; the precipitate is nearly insoluble in dilute acids, but dissolves readily in concentrated hydrochloric acid; on exposure to air whilst moist it gradually oxidises.

A **cobaltoso-cobaltic sulphide**, Co_3S_4, corresponding to the oxide, constitutes the mineral *linnæite* found in Prussia.

244. Cobalt Sulphate, $CoSO_4.7H_2O$, is found native as *cobalt-vitriol:* it may be formed artificially by dissolving the metal, its protoxide, or carbonate in sulphuric acid. It forms red crystals isomorphous with green vitriol. It readily combines with other sulphates to form double salts. A magnesium cobalt sulphate of the composition $3CoSO_4.MgSO_4.28H_2O$ is found native in Hesse: it is sometimes improperly termed "cobalt-vitriol."

245. Cobaltous Nitrate, $Co(NO_3)_2.3H_2O$, is a red crystalline salt of specific gravity 1·83, which melts at 100°, gives off water, and is converted by prolonged heating into the sesquioxide. It is much used in flame reactions.

246. Ammoniacal Cobalt Bases.—On dissolving the hydrated cobalt oxide in ammonia, and exposing the solution to air, oxygen is absorbed, and the liquid becomes brown and ultimately reddish-violet. By the addition of cold hydrochloric acid **roseo-cobaltic chloride**, $Co_2Cl_6.10NH_3.H_2O$, is deposited as a crystalline powder of a brick-red colour, readily soluble in water. When the solution is heated its colour changes from red to violet, and **purpureo-cobaltic chloride**, $Co_2Cl_6.10NH_3$, is formed as a violet or purple crystalline powder, nearly insoluble in cold water, but soluble in hot water acidulated with hydrochloric acid. Many other ammoniacal compounds of cobalt are known, for the details respecting which the larger manuals must be consulted.

Compounds of cobalt impart a splendid blue colour to fused borax. In solution they give a black precipitate with alkaline sulphides. Cobaltous salts give a reddish precipitate of the hydrated oxide on the addition of potash. Ammonia in excess dissolves this precipitate with the formation of a reddish-violet colour. Potassium cyanide produces a reddish-brown precipitate, soluble in excess, forming a green solution. With cobaltic solutions potash gives a black precipitate of the sesquioxide. On mixing concentrated solutions of a cobalt salt and sodium sulphocyanate, a deep-blue colouration is produced, by means of which very minute traces of cobalt may be detected. Potassium ferricyanide gives a blood-red colour, similar to that of the sulphocyanate of iron.

247. Nickel—Symbol Ni; atomic weight 58·7.—This metal was discovered in 1751 by Cronstedt, in the arsenide NiAs, a copper-coloured mineral termed *kupfer-nickel* (*i.e.*, false copper) by the German miners. This compound, together with the impure arsenide termed *speiss*, formed at the bottom of the melting pots in the manufacture of *smalt* (p. 260), constitutes the principal source of nickel. The metal is obtained by reducing its oxide with charcoal at a high temperature. When pure it is white, ductile, and malleable; its specific gravity is 8·3. It melts at about the same temperature as iron, but is more fusible when combined with carbon. It is slightly magnetic at ordinary temperatures, but temporarily loses this property on heating. Nickel alloys readily with the greater number of metals: *packfong*, or *German silver*, is brass (*i.e.*, an alloy of zinc and copper) whitened by the addition of nickel; it is occasionally employed for coinage. Alloys of arsenic and antimony, with nickel, occur native. Articles of brass, copper, and iron, are frequently coated with nickel by electrolytic deposition.

248. Nickel Protoxide, NiO, is occasionally found native: it is formed by igniting the hydrate or carbonate, or by deflagrating the metal with nitre. It is a greyish-green powder, permanent in the air, even when heated; it is reduced to the metal by ignition in hydrogen. The **hydrate,** NiH_2O_2, is obtained by adding potash to a solution of a nickel salt: it is a green powder, soluble in ammonia, forming a violet solution. A crystalline hydrate of nickel oxide, $NiH_2O_2.H_2O$, of an emerald-green colour, has been found native.

249. Nickel Sesquioxide, Ni_2O_3, is a black powder, produced by igniting the nitrate. At a high temperature it evolves oxygen, and is converted into the protoxide. It is obtained hydrated of the composition $Ni_2O_3.3H_2O$, by treating the protoxide, suspended in water, with chlorine, or by adding sodium hydrochlorite to a solution of a nickel salt. It is a brownish-black powder, which evolves water and oxygen on ignition. A hydrate containing 2 molecules of water is formed by the electrolysis of a neutral solution of a nickel salt.

250. **Nickel Chloride,** $NiCl_2$, may be obtained in bright yellow scales, resembling mosaic gold, by heating the metal in chlorine, or by expelling the water from the hydrated salt. By dissolving nickel or its oxide in hydrochloric acid a bright green solution is obtained, which on concentration deposits a crystalline salt of the composition $NiCl_2.9H_2O$. On treating this compound with ammonia, **ammonio-nickel chloride,** $NiCl_2.6NH_3$, is obtained, crystallising in octohedrons possessing a bright blue colour. The **iodide** and **bromide** resemble the chloride, and form similar compounds with ammonia.

251. **Nickel Sulphides.**—A **hemisulphide,** Ni_2S, is obtained as a pale-yellow, shining, fusible mass, by igniting the sulphate in hydrogen.

The **monosulphide,** NiS, occurs native as *millerite* or *capillary pyrites,* of the colour of brass. This sulphide may be obtained artificially by the direct union of its elements, or by heating the oxide either with sulphur or in a stream of sulphuretted hydrogen. A hydrated sulphide is formed by the action of sulphuretted hydrogen on nickel acetate, or by adding ammonium sulphide to a solution of a nickel salt. It is a dark-brown powder, which oxidises when moist: it is slightly soluble in ammonia and ammonium sulphide solutions, to which it imparts a deep-brown colour. A **nickeloso-nickelic sulphide,** Ni_3S_4 or $2NiS.NiS_2$, corresponding to the cobalt mineral *linnæite,* is found native, as *beyrichite.*

252. **Nickel Sulphate,** $NiSO_4.7H_2O$, is obtained in emerald-green crystals, isomorphous with magnesium sulphate, by concentrating a solution of the metal in sulphuric acid. It readily parts with 6 molecules of water on heating, but retains the 7th up to a high temperature. The anhydrous salt is yellow: it absorbs ammonia, forming a violet salt,

$NiSO_4.6NH_3$. A blue-coloured salt of the composition $NiSO_4.4NH_3.2H_2O$ is formed by adding ammonia to a concentrated solution of the sulphate.

253. Nickel Nitrate, $Ni2NO_3.6H_2O$, is an emerald-green salt, also soluble in ammonia, and forming, on concentration, blue octahedral crystals of the composition $Ni2NO_3.4NH_3.xH_2O$.

Nickel salts, heated in the reducing area of the Bunsen flame with sodium carbonate and charcoal, yield the metal as a grey magnetic powder. In the oxidising flame they give to borax a red colour whilst hot, changing to yellow on cooling: on the addition of a potash salt the bead becomes bluish-purple. In solutions containing hydrochloric acid the salts give no precipitate with sulphuretted hydrogen; by the addition of sodium acetate to the liquid nickel sulphide is immediately formed on treatment with the gas. Ammonium sulphide gives the same precipitate, slightly soluble in excess, with the formation of a brown colour. Potash gives the green hydrate, soluble in ammoniacal salts; hence ammonia gives no precipitate with nickel salts in presence of ammoniacal salts. Potassium cyanide forms nickel cyanide soluble in excess. Potassium ferricyanide produces no change in the cold; on boiling, the whole of the nickel is deposited as a copper-red precipitate.

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254. Platinum—Symbol Pt; atomic weight 197·2.—This metal was discovered in 1741 by Mr. Woods, an assayer in Jamaica; its name, signifying *little silver*, is derived from the similarity of its colour to that of silver. Platinum is always found in the metallic state, and generally alloyed with osmium, iridium, rhodium, and palladium. The metal occurs mainly in alluvial deposits, often associated with gold, in small flattened grains of a grey colour. The chief supplies of platinum are obtained from the Urals (Nischni-Taglisk), but the metal is also met with in South America, California, and Borneo.

Platinum is extracted by first treating the ore with nitric acid, to remove any associated copper, lead, or silver, washing it with water, and digesting with hydrochloric acid to dissolve the iron (which principally exists as magnetic oxide), and then heating with nitrohydrochloric acid. The platinum, rhodium, and palladium, and a portion of the iridium, are dissolved; an alloy of osmium and iridium, together with the quartz of the ore, remains undissolved. The solution is then mixed with sal-ammoniac, whereby a precipitate of ammonium-platinum-chloride, $2NH_4Cl.PtCl_4$, is obtained. The precipitate is washed with cold water and heated, ammonium chloride and chlorine are expelled, and the platinum is obtained as a grey spongy mass. The metal is made into a paste with water, consolidated into a cake by pressure, heated to whiteness in a porcelain kiln, and hammered until it is welded into a homogeneous mass, or it is melted in a lime or gas-carbon crucible by means of the oxyhydrogen flame.

Fig. 147 represents the lime furnace of Deville and Debray employed in melting platinum. The blocks of lime, *d* and *e*, are bound together with bands of iron; the metal to be fused is placed in the cavity in *d*, and an oxyhydrogen flame directed upon it; when melted the metal is poured from the lip *a* into the ingot moulds.

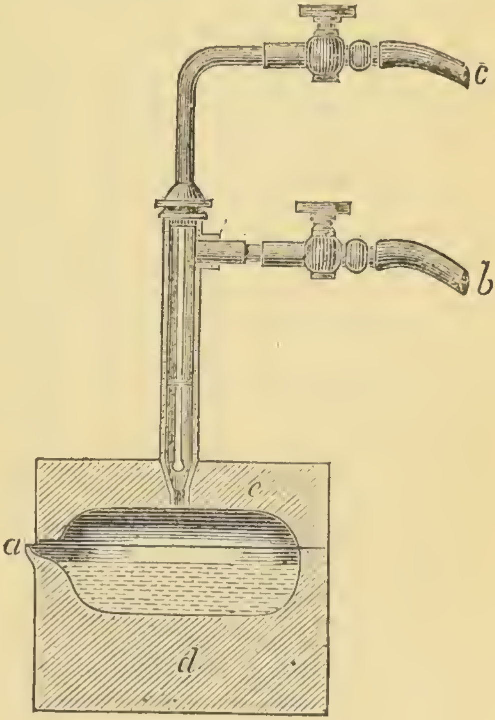


Fig. 147.

In order to extract the platinum, Deville and Debray have proposed to smelt the ore with galena in a reverberatory furnace. A small quantity of glass is added, together with an amount of litharge equal in weight to the galena employed. The oxide and sulphide then react together forming metallic lead and sulphur dioxide; $2PbO + PbS = Pb_3 + SO_2$: the lead dissolves the platinum, whilst the osmium and iridium, being insoluble in lead and specifically heavier than the alloys of lead and platinum, accumulate at the bottom of the molten charge. The platiniferous lead is cast into ingots, and the two metals are separated by cupellation. The spongy mass of platinum left on the cupel is melted in the oxyhydrogen furnace, and is cast into ingot moulds made of gas-coke or of wrought-iron lined with platinum.

Platinum is a white, highly-lustrous metal of great malleability and ductility. It is softer than silver; its specific gravity is about 21·5; it expands but slightly on heating; its coefficient of cubical expansion, according to Dulong, is ·0000265 for 1° C., which is identical with that of glass; hence a platinum wire may be fastened into a glass tube without risk of becoming loose, or of cracking the tube, which would be the case if a wire of copper (co-efficient of expansion ·0000565), or of iron (co-efficient of expansion ·0000441) were used. Air has no oxidising action upon platinum; when fused, however, it absorbs oxygen, which is evolved again as the metal cools. It is scarcely acted upon by any single acid: prolonged boiling with concentrated oil of vitriol appears to dissolve the metal slowly; hence the platinum retorts, employed in the concentration of sulphuric acid on the large scale, are slightly acted upon by long continued use. The best solvent for the metal is nitrohydrochloric acid, which forms the tetrachloride $PtCl_4$. Platinum absorbs or occludes considerable quantities of gas, such as hydrogen and oxygen; if *platinum black*, as the finely-divided metal is termed, be introduced into a mixture of the two gases, combination takes place with such rapidity, and with the development of so much heat, that the gases explode. This property of determining the combination of oxygen and hydrogen is taken advantage of in the well-known Döbereiner's lamp. Platinum black may be readily obtained by exposing an aqueous solution of platinum tetrachloride in an atmosphere of hydrogen to bright sunlight. Finely-divided platinum is used in porcelain painting and in the manufacture of mirrors.

255. **Platinum Monoxide,** PtO or Pt_2O_2, is a black powder, produced by heating the hydrate, formed by the action of potash on the dichloride. It is soluble in acids, and in excess of potash.

Platinum Dioxide, PtO_2, may be obtained by heating the corresponding hydrate, produced by boiling the tetrachloride with a large excess of soda, and adding acetic acid. It is a black powder which, on ignition, is resolved into metal and free oxygen. The hydrate dissolves in acids forming platinic salts; it also unites with bases forming compounds termed **platinates**: they are yellow crystalline powders, obtained by treating the chloroplatinates with the corresponding hydrates.

256. Platinum Dichloride, $PtCl_2$ or Pt_2Cl_4, is a brown powder formed by heating the tetrachloride to 200°. It is insoluble in water and in nitric acid, but dissolves readily in hydrochloric acid: if the solution be exposed to air the salt is gradually converted into the tetrachloride. The solution has a dark-brown colour; with potash it gives a precipitate of platinous hydrate soluble in excess; if alcohol be added to the liquid the whole of the platinum is deposited; with ammonia it forms a green crystalline powder of the composition $2NH_3.PtCl_2$. The dichloride forms double salts with metallic chlorides, termed **chloroplatinites**: they have the general formula M_2PtCl_4. The potassium and ammonium compounds are dark-red crystalline salts soluble in water.

Platinum Tetrachloride, $PtCl_4$, is a dark orange-coloured deliquescent powder, formed by dissolving the metal in nitro-hydrochloric acid. It is highly soluble in water and in alcohol: its solution when pure has a bright-orange colour, but when mixed with iridium, as is usually the case with the commercial salt, its colour is more or less red. On evaporation it yields crystals of the composition $PtCl_4.10H_2O$; when crystallised from solutions containing free hydrochloric acid it forms hydrogen platinochloride, $H_2PtCl_6.2H_2O$. On adding solutions of many chlorides double salts of the general formula M_2PtCl_6 are formed, known as **platinochlorides**. The potassium and ammonium compounds, $(NH_4)_2PtCl_6$ and K_2PtCl_6, are sparingly soluble, yellow crystalline salts; they are of importance as constituting the forms in which potassium and ammonium compounds are most frequently separated in quantitative analysis: the thallium, cæsium, and rubidium salts greatly resemble these compounds, and have an analogous composition; they are even more insoluble in water. Silver chloride is readily soluble in solution of platinum tetrachloride, and may be obtained crystallised therefrom.

Platinic Chloriodide, $PtCl_2I_2$, obtained by the addition of iodine to a solution of the tetrachloride, forms large bright-red deliquescent crystals, melting below 100°.

By the action of sulphurous acid upon ammonium platinochloride, a compound, termed **platino-chlorosulphurous acid**, $PtCl.SO_3H$, is formed.

The production of this body may be represented by the following equations—

$$PtCl_4.(NH_4Cl)_2 + H_2SO_3 + H_2O = PtCl_2 + (NH_4)_2SO_4 + 4HCl.$$

The platinum dichloride thus formed yielding the new acid by the action of a second molecule of the sulphurous acid: thus—

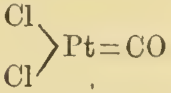
$$PtCl_2 + H_2SO_3 = PtCl.SO_3H + HCl.$$

Platino-chlorosulphurous acid yields a compound with ammonium chloride, crystallising in long orange-yellow prisms of the composition $PtCl.SO_3H.2NH_4Cl$. On adding potassium carbonate to this substance, the H in the group SO_3H is replaced by K: thus—

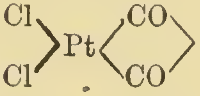
$$PtClSO_3K.2NH_4Cl.$$

By treating potassium platinochloride with sulphurous acid, and adding potassium chloride to the solution, the compound $PtCl.SO_3K.2KCl$ is obtained. Similar compounds containing sodium, calcium, barium, and magnesium have been formed.

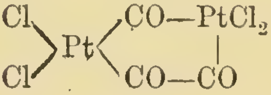
Platino-carbonyl Chlorides.—By passing a stream of carbon monoxide over heated platinum dichloride, a sublimate consisting of a mixture of platino-, mono-, and di-carbonyl dichlorides, and platino-tricarbonyl tetrachloride is obtained. The monocarbonyl chloride crystallises in bright-yellow needles: it melts at 195°, and sublimes at 240°. The dicarbonyl chloride forms white needle-shaped crystals. The tricarbonyl tetrachloride is separated from the mixture by taking advantage of its superior solubility in carbon tetrachloride. Both the dicarbonyl dichloride and tricarbonyl tetrachloride lose carbon monoxide when heated, and pass into the monocarbonyl compound. The constitution of these compounds may be represented by the following formulæ—

Platino-carbonyl dichloride 

$\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}>\mathrm{Pt}=\mathrm{CO}$

Platino-dicarbonyl dichloride 

$\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}>$

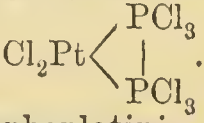
Platino-tricarbonyl tetrachloride 

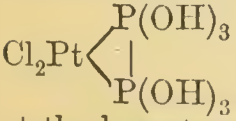
$\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}>\mathrm{Pt}<\begin{array}{ll}\mathrm{CO}-&\mathrm{PtCl}_2\\ &|\\ \mathrm{CO}-&\mathrm{CO}\end{array}$

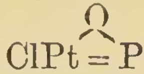
257. Phosphoplatinic Compounds.—When finely-divided platinum and phosphorus pentachloride are heated together to about 250°, a dark claret-coloured crystalline body of the composition $\mathrm{PtCl_2.PCl_3}$ or $\mathrm{Cl_2=Pt=\overset{v}{P}Cl_3}$ is obtained. This substance, which may be termed **phosphoplatinic chloride,** is soluble, without decomposition, in carbon tetrachloride, benzene and its homologues, and chloroform; when gently heated in chlorine it combines with a molecule of that gas, and forms a yellow powder of the composition $\mathrm{Cl_3Pt{-}PCl_4}$. Phosphoplatinic chloride treated with water yields hydrochloric acid and **phosphoplatinic acid,** $\mathrm{Cl_2Pt=P(OH)_3}$:

$$\mathrm{Cl_2Pt.PCl_3+3H_2O=Cl_2Pt.P(OH)_3+3HCl.}$$

By concentrating the solution *in vacuo,* the acid is obtained in orange-red deliquescent prisms.

Phosphoplatinic chloride, dissolved in phosphorus trichloride, yields a crystalline mass of a bright yellow colour, consisting of **diphosphoplatinic chloride,**  $\mathrm{Cl_2Pt}<\begin{matrix}\mathrm{PCl_3}\\ |\\ \mathrm{PCl_3}\end{matrix}$. In contact with cold water it yields **diphosphoplatinic acid,**



$\mathrm{Cl_2Pt}<\begin{matrix}\mathrm{P(OH)_3}\\ |\\ \mathrm{P(OH)_3}\end{matrix}$. By the cautious evaporation of its solution at the lowest possible temperature the acid may be obtained in yellow deliquescent needles. On gently heating, it loses a molecule of hydrochloric acid, and yields a colourless body of the composition $\mathrm{ClP\overset{O}{\overbrace{t=}}P_2(OH)_5}$. By heating to 150°, this substance parts with water, and yields a yellow powder consisting of  $ClPt\overset{\overset{O}{\frown}}{=}P_2O.(OH)_3$.

258. Ammoniacal Platinum Compounds.—On adding excess of ammonia to a boiling solution of platinum dichloride in hydrochloric acid, bright-green needle-shaped crystals of the empirical formula $Cl_2Pt.2NH_3$ are obtained: this substance has long been known as the "green salt of Magnus." If this salt be boiled with a solution of ammonium chloride its colour changes to *yellow*. A *red* or *brownish-red* salt may be obtained by cautiously adding ammonium carbonate to the solution of the platinum dichloride. The green salt of Magnus may be regarded as the chloroplatinate of a base, termed *platoso-diammonium;* according to this view, its composition is $2(Pt(N_2H_6Cl)_2)PtCl_2$. A number of the salts of this base have been prepared: they are perfectly stable compounds, and may be obtained in well-defined crystals. The following list gives the names and formulæ of a few of these salts:—

Platoso-diammonium		chloride	$Pt(N_2H_6)_2Cl_2$
,,	,,	nitrate	$Pt(N_2H_6)_2(NO_3)_2$
,,	,,	sulphate	$Pt(N_2H_6)_2SO_4$
,,	,,	carbonate	$Pt(N_2H_6)_2.CO_3$.

The hydrate of the base, $Pt(N_2H_6)_2(OH)_2$, may be obtained by adding baryta water to the solution of the sulphate and concentrating the filtrate *in vacuo.* It forms a strongly alkaline solid mass resembling potash; it absorbs carbonic acid from the air, expels ammonia from its salts, and forms salts with acid radicles.

A large number of ammonio-platinum compounds have been prepared: all at present known may be considered to be derived from one or other of the groups on p. 273.

The dashes indicate that the groups to which they are attached are unsaturated. This mode of classifying these very complicated compounds is due to Blömstrand; it will be observed that each group, with the exception of the two last, exists in two or more isomeric modifications, in one of which the platinum is assumed to be dyadic (*platoso*), and in the other tetradic (*platino*).

Platoso-ammonium, ... $\overset{\text{II}}{\text{Pt}}\left\{\begin{matrix}\text{NH}_3—\\ \text{NH}_3—\end{matrix}\right.$

Platoso-semidiammonium, ... $\overset{\text{II}}{\text{Pt}}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{———}\end{matrix}\right.$

Platoso-monodiammonium, ... $\overset{\text{II}}{\text{Pt}}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{NH}_3—\end{matrix}\right.$

Platoso-diammonium, ... $\overset{\text{II}}{\text{Pt}}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{N}_2\text{H}_6—\end{matrix}\right.$

Diplatoso-diammonium, ... $\begin{matrix}\overset{\text{II}}{\text{Pt}}\\ |_{\text{II}}\\ \text{Pt}\end{matrix}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \\ \text{N}_2\text{H}_6—\end{matrix}\right.$

Platin-ammonium, ... $=\overset{\text{IV}}{\text{Pt}}\left\{\begin{matrix}\text{NH}_3—\\ \text{NH}_3—\end{matrix}\right.$

Platino-semidiammonium, ... $=\overset{\text{IV}}{\text{Pt}}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{———}\end{matrix}\right.$

Platino-monodiammonium, ... $=\overset{\text{IV}}{\text{Pt}}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{NH}_3—\end{matrix}\right.$

Platino-diammonium, ... $=\overset{\text{IV}}{\text{Pt}}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{N}_2\text{H}_6—\end{matrix}\right.$

Diplatino-diammonium, ... $\begin{matrix}—\overset{\text{IV}}{\text{Pt}}\\ |_{\text{IV}}\\ —\text{Pt}\end{matrix}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \\ \text{N}_2\text{H}_6—\end{matrix}\right.$

Diplatin-ammonium .... $\begin{matrix}—\overset{\text{IV}}{\text{Pt}}\\ —|_{\text{IV}}\\ \text{Pt}\end{matrix}\left\{\begin{matrix}\text{NH}_3—\\ \text{NH}_3—\\ \text{NH}_3—\\ \text{NH}_3—\end{matrix}\right.$

Diplatino-tetradiammonium, ... $\begin{matrix}—\overset{\text{IV}}{\text{Pt}}\\ |_{\text{IV}}\\ —\text{Pt}\end{matrix}\left\{\begin{matrix}\text{N}_2\text{H}_6—\\ \text{N}_2\text{H}_6—\\ \text{N}_2\text{H}_6—\\ \text{N}_2\text{H}_6—\end{matrix}\right.$

259. Platoso-ammonium Chloride, $Pt\left\{\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right.$, is obtained in yellow crystals by adding hydrochloric acid to a solution of platoso-diammonium chloride, or by boiling Magnus' green salt with ammonium chloride (*vide supra*). The corresponding **oxide,** $Pt\left\{\begin{matrix}NH_3\\NH_3\end{matrix}\right\rangle O$, is a grey powder obtained by heating platoso-diammonium hydrate to 110°:—

$$Pt\left\{\begin{matrix}N_2H_6.OH\\N_2H_6.OH\end{matrix}\right. = Pt\left\{\begin{matrix}NH_3\\NH_3\end{matrix}\right> O + 2NH_3 + H_2O.$$

A number of salts corresponding to this oxide have been prepared.

Platoso-semiammonium Chloride, $Pt\left\{\begin{matrix}N_2H_6Cl\\Cl\end{matrix}\right.$, isomeric with the preceding chloride, is formed by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, treating the crystalline powder thus obtained with boiling water, filtering and concentrating the solution. It forms yellow prisms, sparingly soluble in cold water, but readily dissolved by hot water.

Platoso-monodiammonium Chloride, $Pt\left\{\begin{matrix}N_2H_6Cl\\NH_3Cl\end{matrix}\right.$, crystallises in colourless needles: it is very soluble in cold water, and with platinous chloride forms the brownish-red salt obtained by the action of ammonium carbonate on platinum dichloride; hence the composition of this salt is $2\left(Pt\left\{\begin{matrix}N_2H_6Cl\\NH_3Cl\end{matrix}\right.\right).PtCl_2$. It is polymeric with platoso-ammonium chloride, $Pt\left\{\begin{matrix}NH_3Cl\\NH_3Cl.\end{matrix}\right.$

Platoso-diammonium Chloride, $Pt\left\{\begin{matrix}N_2H_6Cl\\N_2H_6Cl\end{matrix}\right.$, is obtained in light-yellow crystals by boiling platinous chloride or the green salt of Magnus with ammonia. When treated with platinous chloride, the latter salt is again formed: this compound is, in fact, the **chloroplatinate of platoso-diammonium chloride,** $2\left(Pt\left\{\begin{matrix}N_2H_6Cl\\N_2H_6Cl\end{matrix}\right.\right).PtCl_2$.

Platin-ammonium Chloride, $Cl_2 = Pt\left\{\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right.$, is formed by the action of chlorine on platoso-ammonium chloride. By the action of silver nitrate, the corresponding nitrate, $(NO_3)_2{=}Pt\left\{\begin{matrix}NH_3NO_3\\NH_3NO_3\end{matrix}\right.$, is obtained; on heating this compound with ammonia, the **hydroxide,** $(OH)_2Pt\left\{\begin{matrix}NH_3.OH\\NH_3.OH\end{matrix}\right.$, is obtained: it is a yellow crystalline powder, unattacked by potash, but readily dissolved by acids with the formation of salts.

Platino-semidiammonium Chloride, $Cl_2Pt\left\{\begin{matrix}N_2H_6Cl\\Cl\end{matrix}\right.$, is formed by the action of chlorine on platoso-semidiammonium chloride. It crystallises in small yellow rhombic tables which are not decomposed by strong sulphuric acid.

Platino-monodiammonium Chloride, $Cl_2Pt\left\{\begin{matrix}N_2H_6Cl\\NH_3Cl\end{matrix}\right.$, is obtained by the action of aqua-regia on platoso-monodiammonium chloride.

Platino-diammonium Chloride, $Cl_2Pt\left\{\begin{matrix}N_2H_6Cl\\N_2H_6Cl\end{matrix}\right.$, is formed by passing chlorine into a solution of platoso-diammonium chloride. It crystallises in light-yellow regular octahedrons. By treatment with silver nitrate only half the chlorine is removed, and a compound of the composition $Cl_2Pt\left\{\begin{matrix}N_2H_6NO_3\\N_2H_6NO_3\end{matrix}\right.$ is obtained. An isomeric body, $(NO_3)_2Pt\left\{\begin{matrix}N_2H_6Cl\\N_2H_6Cl\end{matrix}\right.$, is known; it is formed by the action of hydrochloric acid on a basic **nitrate of platino-diammonium,** $(OH.NO_3).Pt\left\{\begin{matrix}N_2H.NO_3\\N_2H_6NO_3\end{matrix}\right.$. It readily parts with its chlorine on treatment with silver nitrate. For further details concerning the various platino-ammonias and their derivatives, the student is referred to *Watts' Dictionary of Chemistry*, Suppl. II., 992.

260. Platinum Sulphides.—Sulphuretted hydrogen forms the **monosulphide,** PtS, with platinum dichloride; with the tetrachloride it forms the **disulphide,** PtS_2. They are black powders, insoluble in water and acids; the disulphide dissolves in alkaline sulphide forming **sulpho-platinates.**

Platinous compounds give no precipitate with ammonium chloride; platinic salts afford the sparingly-soluble ammonium chloroplatinate. Potash in excess gives no precipitate with platinous salts; with platinic compounds it produces precipitates either of basic salts or of the brown platinic hydrate. Platinous chloride yields the green salt of Magnus on the addition of ammonia.

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261. **Iridium**—Symbol Ir; atomic weight 196·9.—On treating platinum ore with aqua-regia, heavy crystalline scales of a tin-white lustre remain undissolved. These consist of an alloy in variable proportions of iridium and osmium, containing small quantities of the other platinum metals. Its composition is extremely variable, as the following analyses show—sample I. is from Australia; sample II. from the Ural:

	I.	II.
Osmium,	33·46	49·34
Iridium,	58·13	46·77
Rhodium,	3·04	3·45
Ruthenium,	5·22	—
Copper,	0·15	Iron 0·74
	100·00	100·30

Iridosmine, as this mixture is termed, is quite insoluble in any acid or mixture of acids; when heated in the air, the osmium becomes oxidised to osmic tetroxide which volatilises; on heating the alloy with alkaline nitrates, both the osmium and iridium are oxidised and unite with the base.

To obtain the iridium, the alloy is mixed with sodium chloride and heated to redness in chlorine in order to expel the osmium; the mixture is dissolved in water, and the solution of the chlorides again treated with chlorine, mixed with hydrochloric acid and saturated with potassium chloride; a precipitate of the potassio-chlorides of ruthenium, iridium, and platinum is thus obtained: it is dissolved in boiling water, and a current of hydrogen gas passed through the solution; the platinum and ruthenium are first precipitated, and the solution acquires a dark-green colour. The liquid is decanted from the precipitate and again treated with hydrogen when the iridium gradually separates out in extremely thin laminæ possessing a bright metallic lustre.

Iridium may be readily separated from platinum by converting the two metals into their cyanides, combining these with barium cyanide, and picking out the large colourless prisms of the iridium compound from the yellow crystals of the platinum salt.

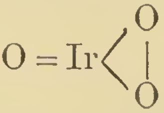
Iridium is now used for many purposes for which platinum was formerly alone employed, as, for example, in the construction of standard weights. To separate the metal on the large scale, the iridosmine is heated with barium nitrate, and the fused mass is treated with water. The residue of iridium oxide and barium osmate is dissolved in nitric acid and distilled to separate the osmic acid. On the addition of caustic baryta to the solution, iridium oxide is precipitated, which is dissolved by aqua-regia, and precipitated as iridiochloride of ammonium by the addition of sal-ammoniac. This compound is ignited, and the spongy metal containing more or less platinum, rhodium, and ruthenium, is heated with nitre; the fused mass is treated with water which extracts potassium rutheniate, and the remaining metals are dissolved by molten lead from which pure iridium gradually separates out.

Iridium, the existence of which was first indicated, independently, by Descotils and by Smithson Tennant in 1803, closely resembles platinum. It is, however, more infusible than that metal and more brittle; its specific gravity is 22·4. It is very slowly acted on by aqua-regia: by mixing it when finely divided with sodium and potassium chlorides, and heating the mixture in a stream of chlorine, potassium and sodium chloriridiates are formed, which are soluble in water.

Four oxides of iridium are known. The **monoxide**, IrO, is an unstable compound readily converted into the dioxide on exposure to air.

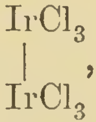
The **sesquioxide**, Ir_2O_3, is a black powder formed by heating a mixture of **potassium chloriridate** ($3KCl.IrCl_3$) and sodium carbonate in carbon dioxide, and treating the mass with water. It is used in porcelain painting as a grey pigment. It may be obtained as a **trihydrate**, $Ir_2O_3.3H_2O$ or IrH_3O_3, by adding potash and alcohol to a solution of the trichloride, or as a **pentahydrate**, $Ir_2O_3.5H_2O$, by adding potash to a solution of an alkaline chloriridite. The oxide gradually absorbs oxygen from the air and passes into the dioxide.

The **dioxide**, IrO_2, is the most stable oxide of iridium. It is obtained as a dark-blue hydrate, $IrO_2.2H_2O$ or IrH_4O_4, by boiling a solution of iridium chloride with an alkali: on heating it is converted into the anhydrous oxide.

The **trioxide**, IrO_3 or  $O=Ir\begin{matrix}\diagup O \\ \vert \\ \diagdown O\end{matrix}$, is obtained in union with potassium by fusing the metal with nitre.

262. Iridium unites with chlorine in three proportions to form a dichloride, a trichloride, and a tetrachloride.

The **dichloride**, $IrCl_2$, is known only in certain double salts termed **hypochloriridites**.

The **trichloride**, Ir_2Cl_6 or  $\begin{matrix}IrCl_3 \\ \vert \\ IrCl_3\end{matrix}$, is obtained by dissolving the corresponding oxide in hydrochloric acid. It combines with certain metallic chlorides to form double salts, known as **chloriridites**, of the general formulæ

$$6MCl.Ir_2Cl_6 \text{ or } IrM_3Cl_6 \text{ and } 3\overset{II}{M}Cl_2.Ir_2Cl_6. \text{ or } \overset{II}{M}_3Ir_2Cl_{12}.$$

The **tetrachloride**, $IrCl_4$, is formed by dissolving the metal, or any of its oxides, in aqua-regia. It is a black deliquescent powder, readily soluble in water. It forms salts with the alkaline chlorides analogous to the chloroplatinates. The potassium compound is soluble in boiling water, and crystallises in dark-red octohedrons.

Iridium forms with ammonia a series of compounds analogous to those of platinum. On treating ammonium chloriridite with a warm solution of ammonia, a compound of the composition

$$10NH_3.Ir_2Cl_6, \text{ or } [N_3H_7Ir(NH_4)_2]_2Cl_6,$$

to which there is no corresponding platinum derivative, is produced. By digestion with silver oxide the base has been obtained as a rose-coloured alkaline mass, of the composition $10NH_3.Ir_2O_3$; the corresponding carbonate, nitrate, and sulphate have also been prepared.

Solutions of iridious salts have a dark olive green colour:

iridic solutions are brownish red. On adding ammonium or potassium chloride to a solution of iridic chloride, the sparingly-soluble chloriridites are obtained as brownish-red crystalline precipitates: on treating their solutions with hydrogen or hydrogen sulphide the colour changes to dark-green.

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263. Lead—Symbol Pb (Plumbum); atomic weight 207.—This metal has been known from very early times: it is mentioned in the book of Job. It was largely smelted in Spain and in this country by the Romans, by whom it was termed *plumbum nigrum.* The alchemists designated it by the sign of Saturn ♄. Metallic lead has been found native in the Kirghiz Steppes in small plates or grains, imbedded in hornstone, and is also met with in certain gold washings. It is principally obtained from the sulphide or *galena,* which is found in Cornwall, Derbyshire, in various parts of Wales, in the Isle of Man, in Saxony, Sweden, and Spain; and from the carbonate or *cerussite,* which occurs associated with galena, in Germany, Spain, and in the United States. Other less important ores are the sulphate, phosphate, and arseniate. To extract the metal the ore is first picked, crushed, and washed, and is then smelted either in reverberatory or blast furnaces. In smelting by the reverberatory furnace the galena is first partially roasted, whereby one portion becomes converted into oxide, with loss of sulphur dioxide; thus, $PbS + O_3 = PbO + SO_2$; and another portion is oxidised to sulphate, $PbS + O_4 = PbSO_4$; the mixed sulphate, oxide, and remaining sulphide then react upon each other, forming metallic lead and sulphur dioxide.

$$\text{(1.)}\ 2PbO + PbS = Pb_3 + SO_2$$
$$\text{(2.)}\ PbSO_4 + PbS = Pb_2 + 2SO_2$$

Fig. 148 represents a longitudinal section, and fig. 149 a plan of the reverberatory or Flintshire furnace, used in smelting galena in this country. The hearth of the furnace is built of fire-bricks, and is lined with grey slag when in a pasty condition, so that it may be fashioned into the hollow shape represented in the figure. The charge, varying from 12 to 30 cwts. of the dressed ore, is introduced through the funnel-shaped aperture or hopper *d*, descending through the arch of the furnace; it is raked over the surface, and is gently heated for a couple of hours,

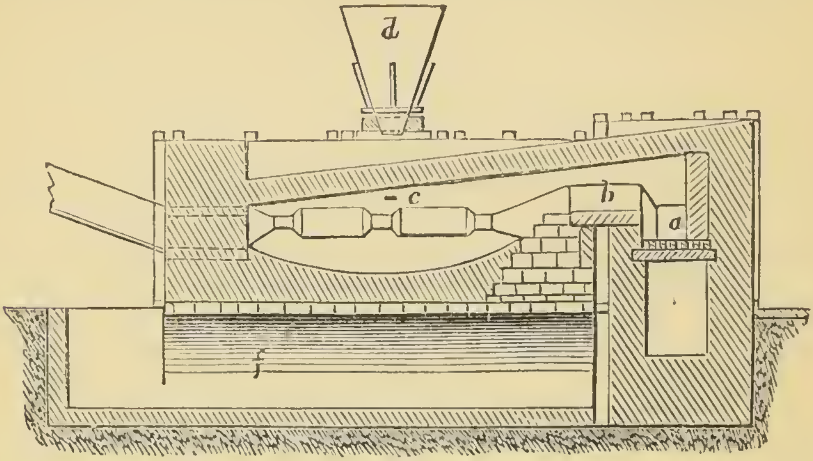


Fig. 148.

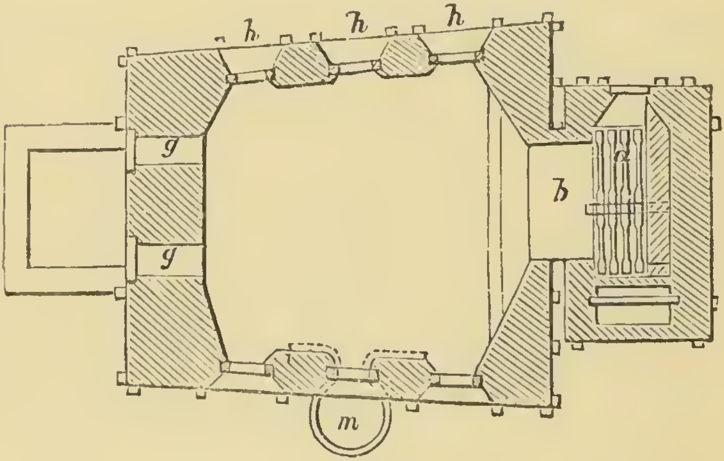


Fig. 149.

care being taken to maintain the temperature below the fusing point of the galena, and to keep the mass constantly stirred. The slags or skimmings, from the surface of the lead in the pot smelted from previous operations, are then thrown into the furnace: a quantity of metal now separates out and runs down into the hollow or well of the furnace, and thence into the metal pot, *m*. The furnace is gradually brought to a full red heat, when the metal runs out in larger amount, and quantities of slag are formed, which are pushed up the slopes of the furnace to allow of the more ready separation of the lead. A few shovelfuls of quicklime are thrown upon the hearth to assist the fluxing. The temperature is again raised, the doors of the furnace being shut; in about an hour the slag is again worked over the hearth, and a larger quantity of quicklime is added to decompose any lead silicate which might be formed, and at the same time to diminish the fusibility of the mixture. The furnace is supplied with fresh fuel and is raised to a high temperature; more lime is added until the slags work dry, when they are raked out in pasty lumps through one of the side doors, after which a second charge is introduced and the above process repeated. The operation of smelting a ton of average ore occupies from five to six hours, and requires from 12 to 16 cwts. of coal. The "grey" slag formed contains occasionally more than half its weight of lead, mainly as oxide: it is therefore re-smelted in the slag hearth.

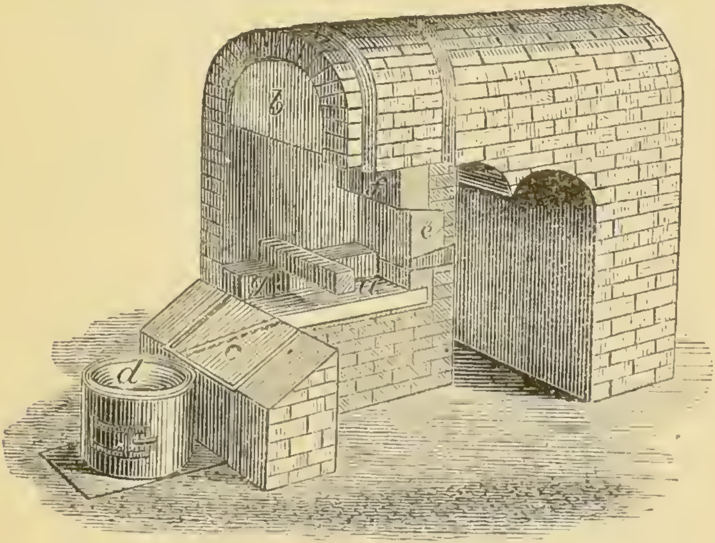


Fig. 150.

In the northern parts of England and in Scotland, lead is smelted in a small blast furnace known as the *ore hearth*, represented in fig. 150. The ore, which is usually previously calcined in a reverberatory furnace, is thrown upon the fire, generally made of a mixture of peat and coal, in quantities of about a dozen pounds at once. The blast issues from a pipe at the back of the furnace, and the mixture is occasionally stirred, so as to loosen the agglutinated ore, or *brouse* as it is technically called, and from time to time portions of the agglomerated mass are drawn on to the fore part of the furnace, or *work-stone*, *c*, and the vitreous or "grey slag" formed is picked out, to be treated in the slag hearth. The oxidised ore, existing partly as sulphate, partly as oxide, reacts upon the sulphide, as previously described, with the separation of the metal, whilst another portion of lead is formed by the reducing action of the fuel; and the metallic lead falls down into the bottom of the furnace; when the hearth is full the metal runs out through a groove cut in the work-stone into the receiving-pot, *d*, from which it is ladled into pig moulds. During the working of the furnace the hearth-bottom is kept constantly filled with melted lead, on which the contents of the ore hearth rest: this bath of molten lead constitutes, indeed, the real bed of the furnace. In smelting, a considerable quantity of lead, partly as oxide partly as sulphide, is mechanically carried away as *fume* by the action of the blast. The lead-fume, together with the other products from the furnace, consisting of gases from the fuel, and sulphur dioxide from the ore, are led through long flues in order that the suspended matter may be deposited; when a sufficient quantity has collected it is smelted in the slag-hearth.

The slag-hearth is a small blast furnace with a single twyer, which enters at the back as in the ore hearth (fig. 151). The bottom, or *bed-plate* of the furnace, which slopes towards the *fire-stone*, *c*, is covered with coarse cinders or coal ashes to within an inch or so from the nozzle of the twyer: this bed acts as a filter to separate the metal produced from the *black* slag simultaneously formed; the lead runs down the bottom of the hearth and into the *lead trough* (*e*) in front, which also is partially filled with cinders; the slag passes into slag-pits (*f*) containing water, where it is broken up by the rapid cooling, so that any lead disseminated through it can be readily extracted by hand-picking or washing. To start it, the furnace is partially filled with peat, a small quantity of burning coal is added, and the blast is turned on. When the furnace is well lighted coke is thrown in, and in about an hour the grey slag or refuse lead-product is added. Fuel and grey slag are added alternately from time to time; the metal separates out, and black slag is formed, to facilitate the flow of which the workman pushes an iron bar beneath the fore-stone into the layer of cinder.

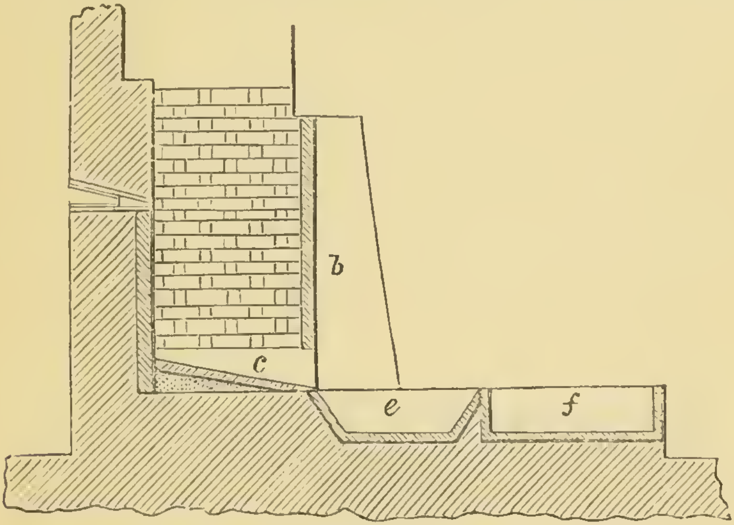


Fig. 151.

The process is mainly one of reduction by the carbonaceous matter of the fuel. A considerable saving is effected by the use of hot air in the blast. The *slag lead*, as the metal thus obtained is termed, is very *hard* or impure, and requires to be softened by the calcining process.

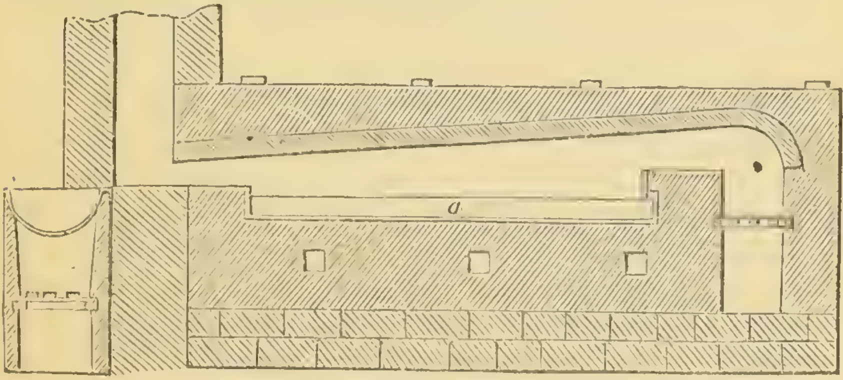


Fig. 152.

Calcining or Improving Process.—The lead obtained from these several operations is frequently so hard, from the presence of antimony, copper, and iron, that it is wanting in malleability—a property upon which the greater number of the applications of lead depend. It is therefore softened by melting it in a shallow pan (a), fig. 152, and exposing it to the oxidising action of the air. The foreign metals, together with a considerable proportion of the lead, being converted into oxides, rise to the surface and are skimmed off, the operation being continued until it is found by trial that the lead is sufficiently soft. The dross, which consists mainly of the oxides of lead and antimony, is afterwards reduced in a reverberatory furnace, and again softened with a fresh quantity of metal; or if the amount of antimony is very large the hard lead is used in the manufacture of type-metal. Various oxidising agents, such as alkaline nitrates and chlorates, have been used to accelerate the softening process, but with only partial success.

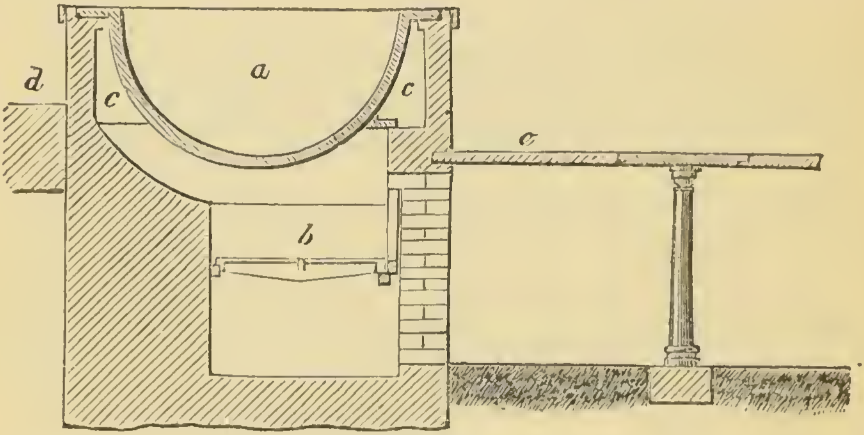


Fig. 153.

Desilvering of lead—Pattinson's process.—Most lead ores, and particularly galena, contain more or less silver, which in the process of reduction finds it way into the lead. If the amount of silver exceeds 10 or 12 ounces per ton, the precious metal may be extracted with profit by cupellation, that is, by melting the lead and oxidising it in the manner described below; the melted litharge flows away, and the silver is eventually left behind on the cupel. Since, however, the greater portion of lead made in this country contains less than this amount of silver, few attempts were made to extract that metal from it. Mr. Pattinson having observed that when an argentiferous lead was melted, the crystals which first formed were comparatively free from silver, from the circumstance that the alloy of lead and silver has a lower solidifying point than the pure lead, conceived the idea of applying the fact to the separation of the two metals. By the process which he introduced, silver is now extracted even though it be present only to the extent of a couple of ounces to the ton. A series of cast-iron pots, the number of which varies in different works, is set in brickwork, and so arranged that each is heated by a separate fire, provided with separate flues and dampers: these pots, known as *working-pots*, contain from 6 to 10 tons of lead (fig. 153). Between each pair of working-pots is placed a small pot, termed a *wash or temper pot,* containing lead heated somewhat above its melting point (fig. 154): in these the perforated ladles, used to remove the lead crystals, are placed whenever the holes of the ladles are stopped up by solidified lead. At the end of the series is the *market pot* in which the desilverised lead is melted, preparatory to being cast into pigs. The ladle used for removing the crystals of lead is seen in fig. 155: it is about 18 inches wide and 6 inches deep, and the entire handle is about 9 feet in length; the perforations are about half an inch wide, and about an inch apart. The process is commenced by melting from 4 to 5 tons of the argentiferous lead in No. 1 pot; as soon as it is perfectly melted the fire is drawn, and the surface of the metal skimmed to remove dross. If necessary, it is cooled to the crystallising point by throwing in a quantity of water, or by adding one or two pigs of lead. The mass of molten metal is then well stirred, and the crystals which form and fall to the bottom of the pot are removed by the perforated ladle and thrown into No. 2 pot. After a time

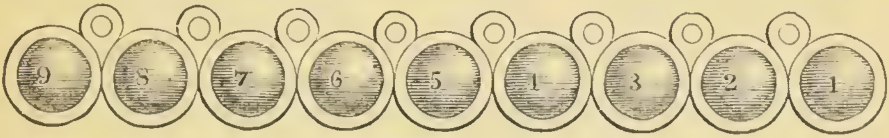


Fig. 154.

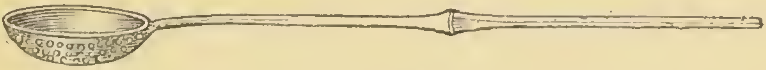


Fig. 155.

the crystals which separate out are found to contain too much silver to be placed in No. 2 pot, they are therefore thrown on to the floor to be remelted with a fresh quantity of lead. When the mass of the lead in No. 1 pot is thus reduced to about one-eighth of its original amount, it is cast into ingots and afterwards cupelled. The contents of No. 2 pot are then melted and subjected to precisely the same treatment, about six-eighths of the quantity are placed in No. 3 pot, an eighth is thrown upon the floor to be remelted with fresh additions from No. 1 pot, and the remaining eighth is put back into No. 1 pot. Pot No. 3 is then treated as pots 1 and 2; the poor crystals being placed in the market pot to be cast into pigs, and the last portion transferred back to No. 3, to be worked up with the fresh quantities from No. 2. By this treatment the amount of silver in the lead is reduced to about one-tenth of its original amount. This method of extraction is termed the method of *eighths*, since the contents of each pot are separated into eight parts, six of which are transferred to the succeeding pot, one being remelted in the same pot, and the remaining enriched eighth being either cupelled or put into the preceding pot. Occasionally, in the case of richer argentiferous lead, the number of pots is greatly increased, as many as fifteen being used, and the method of *thirds* is employed, that is, two-thirds of the contents of a pot are passed on to the succeeding, and one-third transferred to the preceding pot. The following analyses serve to show the general character of the lead after this treatment of calcining and desilverization—

	ENGLISH.	GERMAN. (Villacher).
Lead,	99·9657	99·9870
Copper,	·0236	·0021
Antimony,	·0058	·0052
Silver,	·0010	trace
Iron,	·0021	·0025
Zinc,	·0018	·0032
	100·0000	100·0000

Desilverising with Zinc.—When lead and zinc are melted together, and the mixture allowed to stand, the two metals arrange themselves in layers, of which the upper one consists of zinc containing nearly the whole of the silver originally present in the lead. On account of its higher melting point, the layer of zinc quickly solidifies, and may be detached from the still molten lead. The zinc is used in the proportion of about $1\frac{1}{2}$ lb. of zinc to every ounce of silver, and is well stirred into the molten lead; the alloy, consisting of a mixture of zinc, lead, and silver, is heated in an inclined iron retort *d* (fig. 156); a portion of the lead runs away from it by "liquation," carrying with it a certain portion of the silver which is extracted by cupellation; and the argentiferous zinc is distilled in Belgian retorts with lime and coal, zinc passes over and is condensed, and the silver remains with the residual lead in the retort, from which it is separated by cupellation.

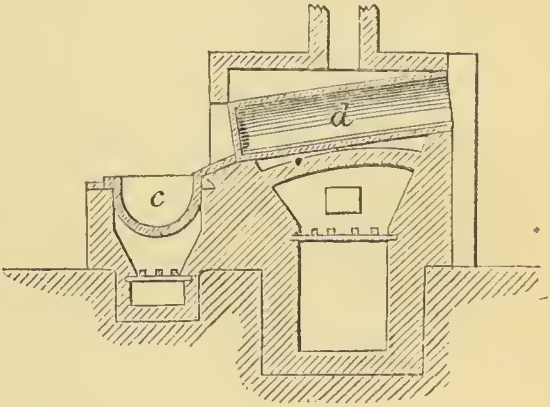
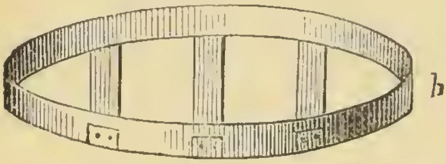
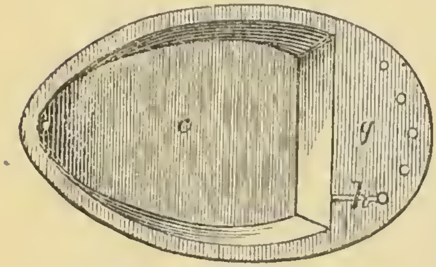


Fig. 156.

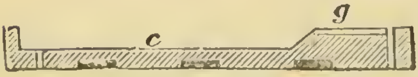
The process of refining is accelerated by blowing steam through the molten metal, the action of the current of vapour being partly mechanical and partly chemical; the antimony is rapidly and completely oxidised, if its quantity does not exceed one-half per cent., and rises to the surface as a scum, which, towards the end of the operation, is found to be rich in copper. Lead crystals separate out from the molten mass, the silver, together with the remainder of the copper, etc., being found in the still liquid portion. In Rozan's process, a quantity of the impure lead is melted in a pot, holding about 10 tons of the metal, and when freed from dross, it is transferred to a second and larger pot; steam is blown in to mix the melted lead with the residue of crystals from a previous operation; water is then sprinkled on its surface to promote crystallization, and the current of the steam is increased, its pressure being about three atmospheres. As soon as about two-thirds of the lead have been deposited, which requires about $1\frac{1}{2}$ hours, the remainder is drawn off; a fresh quantity of impure lead is introduced, and the process is recommenced.



Test Frame.



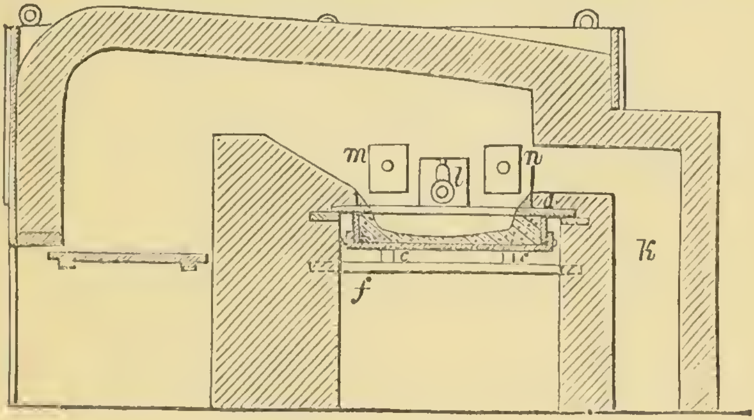
Plan of Test.



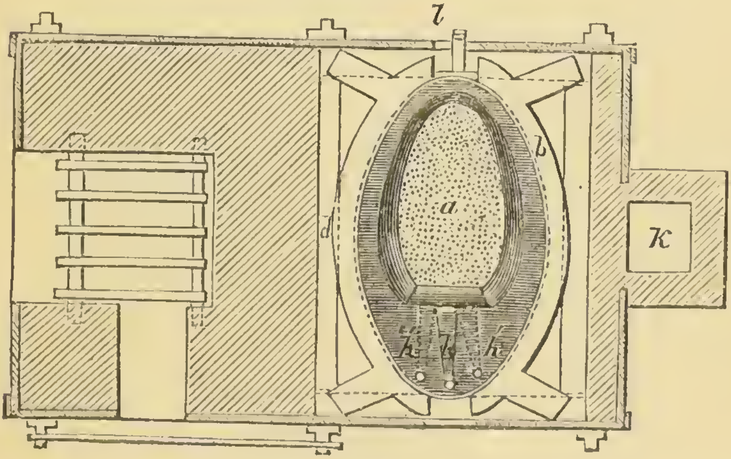
Vertical Section.

Fig. 157.

Refining or Cupellation.—The silver is extracted from the "rich" lead by cupellation. The principle of the process has already been stated: it consists in oxidising the lead by the action of a current of air, and removing the litharge as fast as it is formed; the silver is eventually obtained on the cupel nearly free from lead. Two methods of carrying out the process are used, known respectively as the English and the German methods. In the English method, the hearth upon which the metal is melted consists of an oval iron frame filled with powdered bone-ash, moistened with a solution of pearl-ash: the ash is beaten down and scooped out in the form of a dish (fig. 157). This dish or *cupel* does not completely fill the oval ring, a channel being left for the passage of the melted litharge. The cupel or *test* is then put in position in the furnace, as seen in fig. 158. The flame, from the fireplace in the front of the furnace, passes over the cupel, and the products of combustion make their escape through a flue (*k*) into the chimney. At one end of the cupel is a twyer (*e*), capable of delivering a blast of air at the rate of from 200 to 300 cubic feet a minute. The lead to be refined is melted in an adjoining pot, and run on to the cupel in quantities of about 600 lbs. at once; as soon as the oxidation of the lead commences the blast is turned on, and the litharge, as it is formed, is directed by its action through the channel in the cupel, from which it falls into an iron pot placed to receive it. More lead is added from time to time, until the silver has become concentrated to the extent of about 8 per cent., when a hole is drilled into the bottom of the cupel, and the rich lead runs out into an iron pot; the hole is then stopped up and the process recommenced. The rich alloy is refined in the same manner in a smaller and somewhat differently shaped cupel, until nearly the whole of the lead is removed by oxidation. The second cupellation needs a greatly increased heat, in order to maintain the silver perfectly fluid to the end of the process. What is known as the "brightening" or "fulguration" of the silver, a phenomenon frequently observed in silver assaying, is not generally seen on the large scale, but the formation of little craters, and the consequent spitting of the mass, due to the rapid



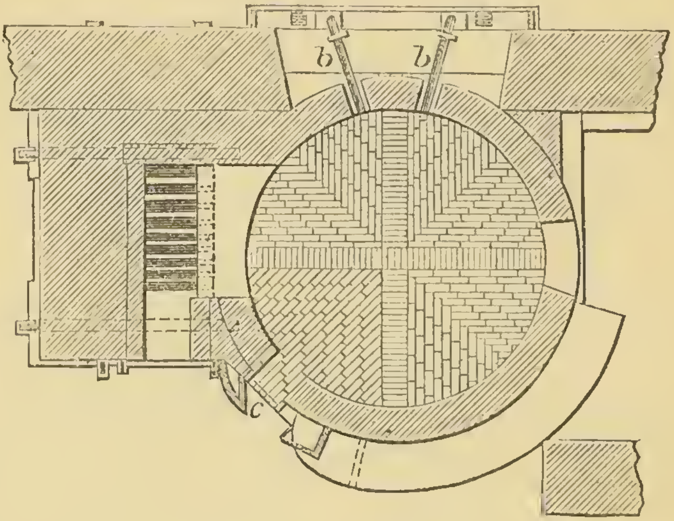
Vertical Section.



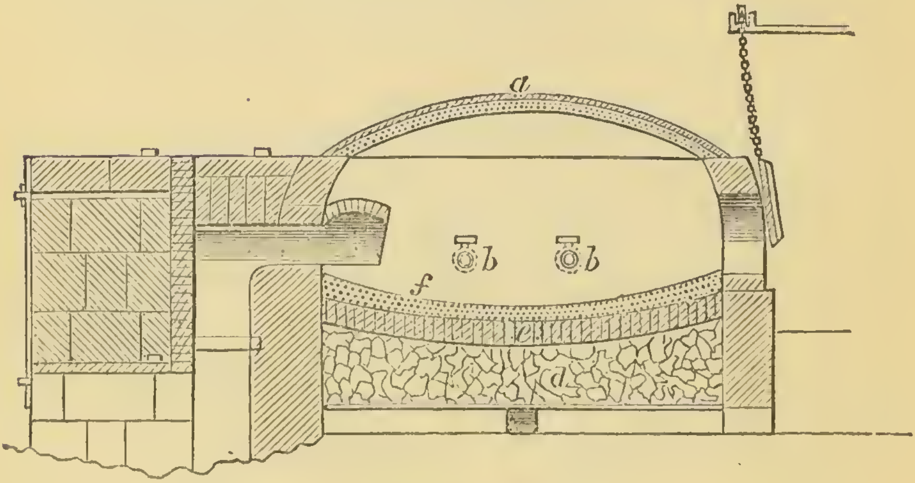
Horizontal Section.

Fig. 158.

disengagement of the dissolved oxygen constantly takes place, and has to be guarded against by perforating the surface of the solidifying metal, in order to facilitate the evolution of the gas.



Plan of the Bed.



Vertical Section.

Fig. 159.

The principle of the German cupellation process is precisely the same as that of the English method, but the construction of the furnace and the composition of the cupel or test are different. Fig. 159 represents a German cupelling furnace. The hearth, which is fixed, is circular, and much larger than in the English furnace; it is lined with marl, or a mixture of dolomite or carbonate of lime and clay. The twyers, generally two in number, are seen at *bb*. About 5 tons of the lead are cupelled at once; soon after melting, a pasty, slag-like mass or scum, termed *abzug* by the Germans, collects on the surface, and is removed by skimming. A coating of impure litharge, containing oxides of iron, zinc, antimony, and other metals, known technically as *abstrich*, now begins to form, and is allowed to flow away through the hole *c*, or is skimmed off. The blast is now turned full on, and a purer litharge is rapidly produced, which also flows out through the hole at *c*. As soon as the whole of the litharge has been removed the metal is quickly cooled by throwing water upon it, the movable head *a* is raised by means of a crane, and the cake of silver is taken from the hearth.

The litharge produced in large quantity in these processes is afterwards reduced in a reverberatory or blast furnace with coal or charcoal.

Lead is a white metal with a characteristic bluish-grey tint; when freshly cut or melted it shows a bright surface, which rapidly tarnishes on exposure to air. It may be obtained in crystals derived from the regular system. It is so soft that it may be scratched with the finger-nail; and it makes a streak when drawn upon paper. It is but slightly elastic or sonorous; it is highly malleable, but cannot be drawn into very thin wire. When heated it may be forced through perforations, a property which is taken advantage of in the manufacture of piping and of rifle-bullets. Lead is about 11·38 times heavier than water: its density is increased by rolling. It melts at about 330°, but cannot be distilled from closed vessels: the lead which is carried away in a current of air exists as oxide.

Lead combines readily with many metals to form definite alloys. *Type-metal* is an alloy of 4 parts of lead and 1 of antimony, and, occasionally, of tin; *stereo-metal* consists of a mixture of lead, tin, and antimony, and, sometimes, bismuth. *Fine solder*, melting at 170°, consists of 2 parts of tin and 1 of lead; *common solder*, melting at 190°, contains equal weights of the metals; and *coarse solder*, melting at 230°, consists of 2 parts of lead and 1 of tin. *Pewter* is composed of 1 part of lead and 4 of tin. *Queen's metal,* used for making spoons, teapots, etc., is a mixture of lead, antimony, and bismuth, with tin.

Shot-metal consists of lead containing from 0·5 to 2 per cent. of arsenic, formed by adding a rich arsenide of lead to molten lead. The molten mass is poured through a metallic sieve down a shaft, and the congealed drops are allowed to fall into a dilute solution of sodium sulphide, whereby they become coated with a thin film of lead sulphide which prevents oxidation. They are afterwards sorted and shaken with powdered graphite.

Lead unites with oxygen in five proportions to form plumbous oxide, Pb_2O, plumbic oxide, PbO, triplumbic tetroxide, Pb_3O_4, diplumbic trioxide, Pb_2O_3, and monoplumbic dioxide, PbO_2.

264. Plumbous Oxide, or **Lead Suboxide,** Pb_2O, is a black powder formed by heating lead oxalate to 300°:

$$2PbC_2O_4 = Pb_2O + CO + 3CO_2.$$

It ignites when heated in the air, and is converted into the monoxide. When heated with a dilute acid, it is resolved into metallic lead and the monoxide which dissolves in the acid.

Plumbic Oxide, PbO, is found native as *lead ochre,* and may be obtained artificially by heating the carbonate or oxalate. *Massicot* and *litharge* consist of the monoxide. Massicot is a yellow powder formed by heating lead to dull redness and removing the film of oxide as it is produced. Litharge is obtained in the cupellation of lead at a high temperature; the melted litharge flows from the cupel into iron pots in which it slowly cools. The mass when cold breaks up into crystalline scales, constituting what is known as *flake litharge;* the coherent pieces are afterwards ground between stones under water, forming *buff* or *levigated litharge.*

Lead monoxide is dimorphous: it may be obtained in regular dodecahedrons or in rhombic octahedrons. Its specific gravity varies slightly with its crystalline form; its mean value is about 9·3. It is sparingly soluble in water, but readily dissolves in acids and the fused alkalies.

265. Plumbic Hydrate, PbH_2O_2, may be obtained as a crystalline precipitate by adding ammonia to a solution of lead nitrate or acetate. When moist it absorbs carbon dioxide from the air; it becomes anhydrous on heating to about 150°.

266. Triplumbic Tetroxide, Minium, or **Red Lead,** Pb_3O_4 or $2PbO.PbO_2$, occurs native, and is obtained artificially by heating the preceding oxide in air. In preparing it on the large scale, about a ton of lead is melted on the hearth of a furnace and exposed to a current of air; the oxide which gradually forms is pushed towards the back of the furnace, and removed to a trough and ground between stones under water; the levigated powder is then reheated to a low temperature for about 48 hours until the proper tint is obtained. Red lead is used extensively as a pigment, and in the manufacture of glass. The name "minium" was originally applied to cinnabar, which was extensively adulterated with red lead: by degrees the name passed to the adulterant. On heating, red lead temporarily darkens in colour, becoming almost black, and at a red heat it loses oxygen and is converted into the protoxide. On treatment with dilute nitric acid the protoxide dissolves and the brown dioxide remains. The tetroxide is perfectly soluble in glacial acetic acid, forming a mixture of acetates. The solution acts as an oxidising agent, decolourising indigo, changing sulphurous acid to sulphuric acid, and oxidising iodine to iodic acid.

Diplumbic Trioxide or **Lead Sesquioxide,** Pb_2O_3, is an orange-red powder obtained by mixing a solution of the preceding oxide in acetic acid with dilute ammonia water. It is decomposed on heating, and is reduced by oxalic acid solution; it dissolves in cold hydrochloric acid, but the solution quickly gives off chlorine, and lead chloride, $PbCl_2$, is precipitated.

Plumbic Dioxide or **Puce Oxide,** PbO_2, is found native as the mineral *plattnerite*, and may be prepared by treating the protoxide or carbonate suspended in water with a stream of chlorine gas, or by the action of nitric acid upon the red oxide. It is reduced on heating or by exposure to sunlight to the red oxide; it becomes heated to redness when projected into sulphur dioxide, and takes fire when triturated with sulphur; it oxidises ammonia to nitric acid, and the reduced oxide is dissolved, forming lead nitrate. On boiling a solution of a manganese salt, free from chlorine, with nitric acid and the brown oxide, permanganic acid is produced. The formation of this acid under these circumstances constitutes an exceedingly delicate test for manganese. The dioxide forms crystallisable compounds with potassium and calcium hydrates.

267. **Lead Chloride**, $PbCl_2$, is readily obtained by adding hydrochloric acid or a soluble chloride to a solution of a lead salt. It crystallises in forms derived from the rhombic system. It is sparingly soluble in cold water (1 part in 120 parts), but is much more soluble in boiling water and in strong hydrochloric acid. It fuses at 501° and gives off fumes, and in contact with air is converted into an oxychloride, $PbO.PbCl_2$, which is found native as *matlockite*, and is made artificially as a pigment by boiling the chloride with milk of lime. *Mendipite* is an oxychloride of the composition $PbCl_2.2PbO$. *Turner's yellow* has the composition $PbCl_2.3PbO$; *Cassel yellow* is $PbCl_2.7PbO$.

268. **Lead Bromide**, $PbBr_2$, resembles the chloride, but is even more insoluble in water than that salt. It combines with the monoxide, forming oxybromides corresponding to the oxychlorides.

269. **Lead Iodide**, PbI_2, is a bright-yellow crystalline powder formed on mixing solutions of lead nitrate and potassium iodide. It dissolves in a large quantity of boiling water; as the solution cools, beautiful spangles of a golden-yellow colour are precipitated. On heating, the iodide becomes dark-red and fuses; at a high temperature it loses iodine and is converted into an oxyiodide. If lead acetate be mixed with potassium iodide an oxyiodide, $PbI_2.PbO$, is formed.

270. **Lead Fluoride**, PbF_2, is a sparingly soluble white salt, obtained by adding hydrofluoric acid to a solution of lead acetate.

271. **Lead Monosulphide** or **Galena**, PbS, constitutes the most abundant ore of the metal. It forms leaden-grey cubical crystals; other forms derived from the regular system are occasionally met with. The sulphide may be formed artificially by fusing lead and sulphur together, or by passing sulphuretted hydrogen through solutions of lead salts. It

melts at a bright-red heat, and, out of contact with air, may be volatilised unchanged. When boiled with moderately dilute nitric acid, it forms lead nitrate, with the liberation of sulphur; if the acid be strong, lead sulphate is formed. By passing sulphuretted hydrogen into a solution of lead chloride a **sulphochloride**, $PbCl_2.3PbS$, of a red colour is formed; excess of sulphuretted hydrogen converts it into lead sulphide.

Lead Sulphate, $PbSO_4$, is found native as the mineral *anglesite:* it is formed as a heavy white crystalline powder by mixing solutions of a lead salt and sulphuric acid or a sulphate. It is almost insoluble in pure water, slightly more soluble in the mineral acids, and readily soluble in solutions of ammoniacal salts, caustic potash and soda, and sodium thiosulphate. It melts at a red heat, and on heating with the sulphide forms metallic lead and sulphur dioxide. The mineral *lanarkite*, occurring in the Leadhills in Scotland, is a compound of sulphate and oxide of lead, $PbSO_4.PbO$.

272. **Diplumbic Nitrite**, $Pb_2HO_2.NO_2$, is a bright-red crystalline powder formed by boiling a solution of the nitrate with metallic lead. By treating a solution of this salt with carbonic acid the **normal nitrite**, $Pb2NO_2$, is obtained in yellow prisms easily soluble in water. A number of nitroso-nitrates or double salts of nitrites and nitrates of lead are known.

273. **Lead Nitrate**, $Pb2NO_3$, is readily obtained by dissolving the metal or the monoxide in nitric acid. It forms milk-white octahedrons, soluble in about 7 parts of cold water. On heating, it is decomposed into lead monoxide, oxygen, and nitrogen tetroxide. It forms a number of basic salts sparingly soluble in water.

274. **Lead Orthophosphate**, $Pb_3P_2O_8$, is a white powder formed by mixing solutions of lead acetate and sodium phosphate. It forms double salts with lead nitrate and chloride. *Pyromorphite*, $2Pb_3P_2O_8.PbCl_2$, is found in hexagonal prisms in Cumberland, Scotland, the Hartz, and other localities; the isomorphous mineral *mimetesite* has an analogous composition, the phosphorus being replaced by more or less arsenic.

275. **Lead Carbonate**, $PbCO_3$, as the mineral *cerussite*, constitutes an important ore of the metal. It is found in rhombic crystals isomorphous with witherite. It sometimes

occurs associated with the chloride, forming *kerasin* or *horn-lead*, $PbCl_2.PbCO_3$. On mixing solutions of alkaline carbonates and lead salts, precipitates are obtained, the composition of which varies with the relative proportion of the reacting salts and the temperatures of the solutions. The *white lead* of commerce is a mixture of lead carbonate and hydrate in variable proportions: its normal composition may be expressed by the formula $2PbCO_3.PbH_2O_2$. White lead is made according to what is known as the *Dutch process*, by placing rolls of sheet lead in earthenware crucible-shaped vessels containing a small quantity of dilute acetic acid, and surrounding them with fermenting tan in the manner indicated in fig. 160. The basic acetate formed by the action of the acid on the metal is rapidly converted into carbonate by the carbonic acid liberated from the decomposing organic matter; the acetic acid thus set free again acts upon the metal until the whole is converted into the carbonate. This method is imitated in Germany by suspending thin plates of lead in chambers containing the vapours of acetic acid and water, and subsequently introducing carbon dioxide and air. In the *quick process*, litharge is suspended in a solution of lead nitrate or acetate, and treated with carbonic acid.

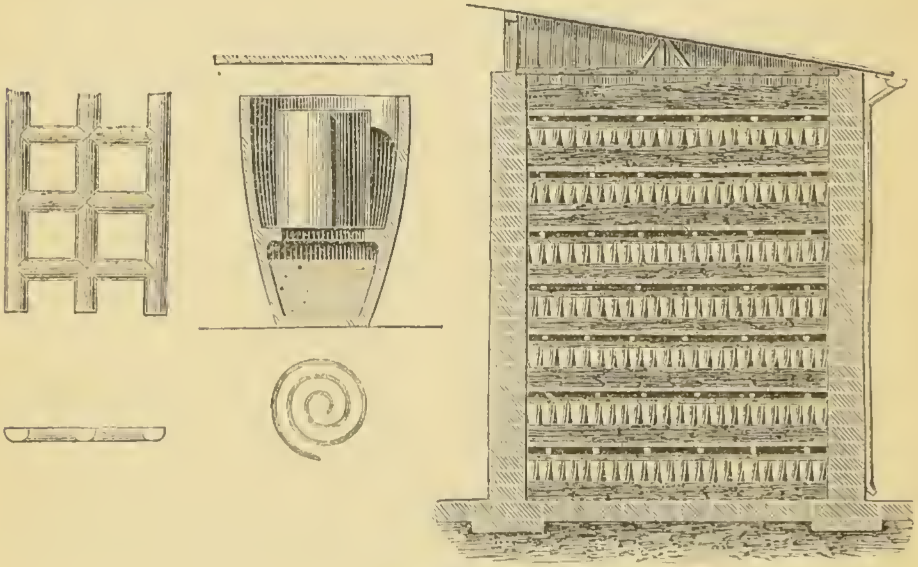


Fig. 160.

276. Lead Silicate is obtained as a yellow glass by fusing the monoxide with silica. Faraday's *heavy glass* is a **borosilicate of lead** made by fusing a mixture of 112 parts of lead oxide, 16 of silica, and 24 of boron trioxide.

Compounds of lead are readily reduced on heating with charcoal in the reducing area of the Bunsen lamp, and yield soft malleable globules of the metal. In solution, salts of lead give with sulphuretted hydrogen the black sulphide, oxidised to insoluble sulphate on heating with strong nitric acid; with hydrochloric acid they yield the chloride sparingly soluble in cold water, more soluble in hot water; with sulphuric acid they give a dense precipitate of the sulphate, soluble in sodium thiosulphate; caustic potash throws down the hydrate, soluble in excess of the precipitant; potassium iodide gives the yellow iodide.

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277. **Thorium** or **Thorinum**—Symbol Th; atomic weight 234, Cleve; 231·4, Delafontaine. This rare element was discovered by Berzelius in 1828 in *thorite*, a hydrated thorium silicate, found in the Norwegian island of Lövön. It has also been met with in the minerals *euxenite*, *gadolinite*, and *orthite*. The metal is obtained by heating the chloride with sodium as an iron-grey powder of specific gravity 7·8, permanent in the air at ordinary temperatures, but burning with great brilliancy when heated, forming the only known oxide **thoria**, ThO_2. This substance is a white powder, which, after treatment with nitric or hydrochloric acid, becomes brownish-red and translucent; it is perfectly soluble in water, but gives a solution which, by reflected light, appears like thin milk and water. The thoria in the solution is apparently in a condition resembling that of colloidal silica; when dried over sulphuric acid it has the appearance of opal. The **hydrate**, ThH_4O_4, is obtained as a gelatinous precipitate by adding potash to a solution of a thorium salt.

278. The **chloride**, $ThCl_4$, is prepared by igniting a mixture of thoria and charcoal in chlorine. It is a white crystalline, highly deliquescent powder, which may be volatilised without change, and is readily dissolved by water and alcohol. It forms double salts with many metallic chlorides.

279. The **sulphate**, $Th(SO_4)_2.9H_2O$, crystallises in forms derived from the triclinic system. It is sparingly soluble in water, and forms double salts with the alkaline sulphates of the general formula $Th(SO_4)_2.M_2SO_4$. The **nitrate**, $Th(NO_3)_4.12H_2O$, is obtained in large transparent hygroscopic tables by evaporating a solution of the hydrate in nitric acid.

In the general character of its reactions, thorium closely resembles zirconium and certain of the cerite metals. It is distinguished from zirconium by the formation of a white precipitate with potassium ferrocyanide. Potassium-thorium sulphate is insoluble in solution of potassium sulphate; the corresponding yttrium salt dissolves in that solution. Sodium thiosulphate gives a precipitate with thorium salts, but not with compounds of the cerium metals.

CHAPTER IX.

GROUP V.—PENTAD METALS.

NIOBIUM. TANTALUM. VANADIUM.

THE atomic value of niobium and tantalum is inferred from the vapour densities of their chlorides which agree with the formulæ $NbCl_5$ and $TaCl_5$. On the other hand, oxyfluoride of niobium, $NbOCl_3$, forms a series of double salts with certain metallic fluorides which are isomorphous with the corresponding stanno-, zircono-, and titano-fluorides, and also with the tungsto-fluorides; in other words, isomorphous salts are formed by tin, titanium, and zirconium, which are tetrads, niobium which is a pentad, and tungsten which is a hexad; a fact which seems to show that identity of crystalline form between corresponding derivatives of two or more different elements cannot be taken as definitely indicating identity of atomic value in the elements. (Compare p. 162, Vol. I.)

Vanadium may be supposed to stand to niobium in the same relation in which, among the tetrads, titanium stands to zirconium. In many respects, however, vanadium is closely related to arsenic and phosphorus: its atomic weight is nearly midway between those of the two latter bodies, thus $\frac{31+75}{2}=53$; and the similarly constituted minerals *pyromorphite*, $Pb_5(PO_4)_3Cl$, *mimetisite*, $Pb_5(AsO_4)_3Cl$, and *vanadinite*, $Pb_5(VO_4)_3Cl$, are isomorphous. Moreover, the difference between the specific volumes of phosphoryl and vanadyl trichlorides is of the same order as that between the correlated tetrachlorides of tin and titanium. Lastly, in vanadium dichloride and in vanadyl dichloride, vanadium would appear to have an even atomic value, unless these compounds be formulated as V_2Cl_4 and $V_2O_2Cl_4$; at present we have no means of deciding upon their true molecular weights. In the tetrachloride, however, vanadium would appear to be distinctly tetradic, since the vapour density of this compound agrees with the formula VCl_4. (Compare p. 30).

280. Niobium—Symbol Nb; atomic weight 94.—This element was discovered by Hatchett in a mineral termed *columbite*, and hence it was originally called columbium. The name which it now bears was assigned to it by Rose. Columbite or *niobite* is a niobate of iron and manganese, $FeNb_2O_6$, analogous to tantalite. *Polycrase* and *euxenite* are mixtures of metallic titanates and niobates: *samarskite* is a niobate of uranium, yttrium, and iron: *æschynite* is a mixture of niobates, titanates, and thorates of cerium, lanthanum, calcium, and iron. Metallic niobium has not yet been described.

Niobium combines with oxygen in three proportions to form NbO, NbO_2, and Nb_2O_5.

281. The **protoxide**, NbO, is a black powder, and was formerly mistaken for the metal. It may be obtained by igniting the double fluoride of niobium and potassium with potassium in presence of air, or, better, by heating the oxychloride with magnesium.

The **dioxide**, NbO_2, is formed by strongly heating the pentoxide in hydrogen. It is a black powder which is reconverted into the pentoxide by heating in air.

The **pentoxide**, Nb_2O_5, is a white powder which becomes temporarily greenish-yellow on heating. Its specific gravity is about 4·5. It may be obtained hydrated, $N_2O_5.7H_2O$, by boiling sodium niobate with dilute sulphuric acid. It is completely insoluble in acids after ignition. When heated in ammonia gas it yields a nitride; vapour of carbon disulphide converts it into an oxysulphide. Niobic acid combines with metallic oxides, forming complex series of salts. For example, four potassium niobates are known, viz :—

$4K_2O.3Nb_2O_5.16H_2O.$
$8K_2O.7Nb_2O_5.32H_2O.$
$3K_2O.2Nb_2O_5.13H_2O.$
$K_2O.3Nb_2O_5.5H_2O.$

282. **Niobium Pentachloride**, $NbCl_5$, is a yellow fusible solid formed by passing chlorine over a heated mixture of the pentoxide and charcoal. An **oxychloride**, $NbOCl_3$, and an **oxyfluoride**, $NbOF_3$, are also known. The latter compound combines with alkaline fluorides to form a series of well-crystallised double salts.

A carbo-nitride (cyanide?) of niobium is obtained in long greyish-violet needles by igniting a mixture of niobic acid, carbon, and sodium carbonate in air; its composition is unknown.

For the reactions of niobium, see Tantalum, p. 301.

283. **Tantalum**—Symbol Ta; atomic weight 182.—The existence of this element was first indicated by Hatchett in 1802. It is found in two minerals named *tantalite* and *yttrotantalite*. The former is a ferrous and manganous tantalate; the latter is a tantalate of yttrium. It is also found associated with niobium in *columbite* or *niobite*. The metal is obtained as a black powder of specific gravity 10·8, by heating sodium fluotantalate with metallic sodium in an iron crucible. It burns when heated in air, forming tantalic oxide, and is not attacked by any of the strong mineral acids, with the exception of hydrofluoric acid.

284. **Tantalum Dioxide**, TaO_2, or Ta_2O_4, is a dark-grey lustrous powder, of great hardness, formed by reducing the pentoxide by means of carbon at a high temperature.

Tantalum Pentoxide, Ta_2O_5, is a white powder, of specific gravity 7·4, which may be obtained in needle-shaped crystals by fusion with microcosmic salt. It is perfectly insoluble in water and acids, and is neither fusible nor volatile, even at the highest temperatures. Heated in ammonia gas it forms the nitride; and with vapour of carbon disulphide it produces the disulphide. By fusion with alkalies or their carbonates it yields **tantalates**, the general formula of which is $M_2OTa_2O_5$.

285. **Tantalum Pentachloride**, $TaCl_5$, is formed by heating the metal in chlorine gas, or by heating a mixture of the dioxide and charcoal in chlorine. It forms a yellow crystalline mass; it melts at 211·3°, and boils at 241·6° under a pressure of 753 mm. It is slowly decomposed by water; more rapidly in presence of ammonia.

Bromine forms a similar compound.

286. **Tantalum Fluoride**, TaF_5, is formed by dissolving tantalic acid in aqueous hydrofluoric acid. When mixed with alkaline fluorides it forms crystallisable double salts, termed **fluotantalates**, of the general formula $M_2Ta_2F_7$.

Tantalum resembles niobium in its reactions. Before the blowpipe niobic oxide gives, with microcosmic salt, a colourless bead in the oxidising flame, becoming purple or blue in the reducing flame, and changing to blood-red on the addition of a trace of a ferrous salt. This reaction is not given by oxides of tantalum. The soluble niobates give, with hydrochloric acid, a white precipitate insoluble in excess : with the tantalates this acid gives a similar precipitate, soluble in excess; potassium ferrocyanide gives a red precipitate with the niobates and a yellow precipitate with the tantalates: with potassium ferricyanide the precipitate formed by the niobates has a bright yellow colour : with the tantalates it is white. Infusion of galls gives an orange-red precipitate with the niobates and a light-yellow precipitate with the tantalates.

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287. **Vanadium**—Symbol V; atomic weight 51·3.—This element was discovered by Sefström in 1830, in the metallic iron and refinery slags obtained from certain Swedish iron

ores. It is found associated with lead, zinc, and copper as vanadate, or sometimes as phosphate of vanadium. Certain clays also appear to contain small quantities of vanadium, and it has been met with in meteorites. The metal is obtained as a crystalline powder of a silver-white lustre, by heating the dichloride in a stream of hydrogen gas. Its specific gravity is 5·5. When heated in oxygen it takes fire and forms the pentoxide V_2O_5. It ignites in chlorine, forming the tetrachloride; and when heated in nitrogen it is converted into the mononitride. It is not attacked by hydrochloric acid; strong sulphuric acid, when heated, dissolves it to a yellow liquid, and nitric acid rapidly oxidises it, forming a deep blue solution.

Vanadium forms five oxides, analogous in composition to the oxides of nitrogen.

288. **Vanadium Monoxide,** V_2O, is formed by the gradual oxidation of the metal. It is a brown powder, which gradually passes into the higher oxides on exposure to air.

The **dioxide,** V_2O_2, may be obtained by the action of potassium upon the higher oxides; or, in solution, by the action of nascent hydrogen evolved on dissolving zinc, cadmium, or sodium-amalgam, in a solution of vanadium pentoxide in sulphuric acid. The light-yellow solution of the pentoxide, under the reducing action of the hydrogen flame, passes through various shades of blue and green, and ultimately acquires a lavender tint. This solution of the dioxide is exceedingly unstable; it rapidly absorbs oxygen from the air, and discharges vegetable colours as quickly as chlorine.

The **trioxide,** V_2O_3, is prepared by heating the pentoxide in hydrogen, or by reduction with charcoal. It is a black powder, which gradually absorbs oxygen from the air passing into the tetroxide; if gently heated it glows, and is converted into the pentoxide. It is insoluble in acids, but may be obtained in solution by the action of nascent hydrogen, evolved by means of magnesium, upon a solution of the pentoxide in sulphuric acid. Its salts in solution have a green colour.

The **tetroxide,** or **hypovanadic oxide,** V_2O_4, is a dark-green amorphous powder, and is easily obtained in solution, forming a deep blue liquid, by the reducing action of oxalic acid, or sulphurous acid upon the sulphuric acid solution of the pentoxide. On the addition of sodium carbonate the hydrate, $V_2O_47H_2O$, is obtained as a black amorphous mass. The oxide in solution acts as a feeble acid, giving rise to a series of unstable salts termed **hypovanadates.** It also combines with acid radicles. The solution of the oxide in sulphuric acid, when evaporated to a syrup and mixed with strong oil of vitriol, yields a vanadic sulphate of a pale-blue colour of the formula $V_2O_4.3SO_3.6H_2O$. A number of other sulphates of a similar character have been obtained.

The **pentoxide,** V_2O_5, the highest oxide and best known member of the series, is obtained by the action of nitric acid upon the lower oxides. It may also be prepared by igniting ammonium vanadate, or by the action of water upon vanadyl trichloride. The latter process yields it as a reddish-yellow or brown powder: on heating it readily fuses to a dark-red liquid, which glows on cooling, forming, when pure, a highly crystalline mass. The oxide is but slightly soluble in water: it dissolves in the strong acids, forming yellow solutions.

Vanadic acid gives rise to a series of salts analogous to the phosphates. Many of these occur native, *e.g.*, *vanadinite*, a combination of orthovanadate of lead with chloride of lead, $3(Pb_3VO_4).PbCl_2$, corresponding to *pyromorphite*, $3(Pb_3PO_4).PbCl_2$, and *mimetisite*, $3(Pb_3AsO_4.)PbCl_2$; it may be formed artificially by melting a mixture of lead oxide, lead chloride, and vanadium pentoxide, beneath a flux of common salt. The mineral *descloizite* is a diplumbic vanadate, $Pb_2V_2O_7$, analogous to lead pyrophosphate. Lead metavandate also occurs native, as *dechenite*, $Pb(VO_3)_2$. *Pucherite*, $BiVO_4$, is found in Saxony, and occurs in reddish-brown rhombic crystals.

Roscoelite is a compound of aluminium vanadate and potassium silicate of the formula

$$2(Al_2O_3.V_2O_5).2K_2O.9SiO_2.H_2O.$$

It occurs in California in foliated talc-like masses of a greenish-grey colour.

Mottramite is found as a thin crystalline incrustation of a black colour on the keuper sandstone of Cheshire; its composition may be expressed by the formula

$$(PbCu)_3V_2O_8.2(PbCu).(OH)_2,$$

analogous to that of *dihydrite*, $Cu_3P_2O_8.2Cu(OH)_2$, and of *erinite*, $Cu_3As_2O_8.2Cu(OH)_2$.

Ammonium Metavanadate, NH_4VO_3, is a sparingly soluble crystalline salt formed by adding excess of ammonia to solutions containing the vanadates of potash or soda. On ignition, it leaves pure vanadic acid. It is worthy of note that the soluble vanadates of the three classes, meta-, ortho-, and pyro-, exhibit an order of stability which is the reverse of that of the corresponding phosphates, the metavanadates being the most stable in solution, and the ortho- salts the least stable.

The vanadates of thallium have been more particularly studied by Carnelley, who has obtained the following compounds :—

Tetravanadate,......	$Tl_{12}V_4O_{16}$	or $6Tl_2O.2V_2O_5=4Tl_3VO_4$....	Orthovanadate
Hexavanadate,......	$Tl_{12}V_6O_{21}$	or $6Tl_2O.3V_2O_5=3Tl_4V_2O_7$....	Pyrovanadate
Octavanadate, ...	$Tl_{12}V_8O_{26}$	or $6Tl_2O.4V_2O_5=2Tl_6V_4O_{13}$...	β-vanadate
Decavanadate, ...	$Tl_{12}V_{10}O_{31}$	or $6Tl_2O.5V_2O_5=Tl_{12}V_{10}O_{31}$..	γ-vanadate
Dodecavanadate,....	$Tl_{12}V_{12}O_{36}$	or $6Tl_2O.6V_2O_5=12TlVO_3$....	Metavanadate
Tetradecavanadate,..	$Tl_{12}V_{14}O_{41}$	or $6Tl_2O.7V_2O_5=Tl_{12}V_{14}O_{41}$..	δ-vanadate

β-sodium vanadate or octovanadate, $Na_{12}V_8O_{26}$, corresponding to Fleitmann and Henneberg's sodium phosphate (1), (see p. 379, Vol. I.), is a white crystalline mass difficultly soluble in cold water. The corresponding silver compound is a dark yellow crystalline powder almost insoluble in water.

289. **Metavanadic Acid**, HVO_3, is formed in beautiful golden scales by adding a solution of ammonium vanadate to a saturated solution of copper sulphate mixed with a solution of ammonium chloride and heating to 75°. It is highly hygroscopic, and, when heated, loses water, and is converted into the pentoxide.

290. Vanadium combines with chlorine to form three chlorides, VCl_2, VCl_3, VCl_4.

The **dichloride**, VCl_2 or V_2Cl_4, is a bright-green powder formed by passing the vapour of the tetrachloride mixed with hydrogen through a red-hot tube. By the prolonged action of the hydrogen it is reduced to metallic vanadium. It is hygroscopic, and dissolves in water, forming a lavender-coloured solution.

The **trichloride**, VCl_3, is formed by the spontaneous decomposition of the tetrachloride. It forms purple-coloured shining crystals, which deliquesce on exposure to moist air, producing a brown liquid which, on the addition of a drop of hydrochloric acid, turns green.

The **tetrachloride** is produced by the action of chlorine upon metallic vanadium or upon the mononitride. It is a reddish-brown liquid of specific gravity 1·858, boiling at 154°, with partial decomposition into the trichloride and free chlorine. The tetrachloride is decomposed by water with the formation of a blue solution containing **hypovanadic chloride**, $V_2O_4Cl_2$.

Vanadyl Trichloride, $VOCl_3$, is best prepared by the action of chlorine upon the trioxide:

$$3V_2O_3 + 6Cl_2 = 4VOCl_3 + V_2O_5.$$

It is also obtained, mixed with more or less vanadium tetrachloride, by heating a mixture of the pentoxide and charcoal in a stream of chlorine. It is a light-yellow liquid of specific gravity 1·86527 at 0°, compared with water at 4°, and boils at 127·2. It fumes strongly in moist air with the formation of a reddish cloud of vanadic acid, and is decomposed by water with the production of hydrochloric and vanadic acids.

Vanadyl Dichloride, $VOCl_2$ or $V_2O_2Cl_4$, is a light-green crystalline body of specific gravity 2·88, formed by the action of zinc upon vanadyl trichloride at a high temperature.

Vanadyl Monochloride, $VOCl$ or $V_2O_2Cl_2$, is a brown solid substance formed, together with the preceding substance, by passing a mixture of the trichloride and hydrogen through a red-hot tube.

Divanadyl Monochloride, V_2O_2Cl or $V_4O_4Cl_2$, is formed by the prolonged action of hydrogen upon the preceding compounds. It is a shining metallic powder, having the appearance of mosaic gold.

291. **Vanadium Tribromide**, VBr_3, is a black amorphous body formed by passing bromine vapour over the heated mononitride. It is exceedingly unstable, decomposing even at ordinary temperatures.

Vanadyl Tribromide, $VOBr_3$, is formed by the action of bromine upon the trioxide. It is a dark-red liquid which decomposes on boiling at the ordinary pressure into bromine, and under the atmospheric pressure into

Vanadyl Dibromide, $VOBr_2$ or $V_2O_2Br_4$, a yellowish-brown solid, which deliquesces on exposure to air, forming a blue liquid.

292. **Vanadium Tetrasulphide,** V_2S_4, is a black solid formed by heating the tetroxide in sulphuretted hydrogen. It is insoluble in hydrochloric and sulphuric acids and in solutions of the alkaline sulphides. It burns when heated in the air, forming vanadium pentoxide and sulphur dioxide. It is obtained as a hydrate by adding hydrochloric acid to a solution of a salt of the tetroxide in an alkaline monosulphide.

Vanadium Pentasulphide, V_2S_5, is formed as a hydrate by adding hydrochloric acid to a solution of vanadic acid in an alkaline monosulphide. It is a dark-brown powder which dissolves in aqueous solutions of alkaline hydrates, carbonates, and sulphides, with the formation of reddish-brown solutions.

293. **Vanadium Mononitride,** VN, is obtained by decomposing vanadyl trichloride by ammonia gas and strongly heating the saline mass, or by igniting ammonium metavanadate, or the dichloride, or the trioxide, in a current of ammonia gas. It is a greyish-white powder, and is permanent in the air.

The **dinitride,** VN_2 or V_2N_4, is a black powder formed by heating the white saline mixture obtained by the action of ammonia upon vanadyl trichloride to a moderately high temperature.

Compounds of vanadium give a bright-green colour to borax or microcosmic salt in the reducing area of the non-luminous flame.

Solutions of hypovanadic oxide have a blue colour. On the addition of potash or its carbonate, a greyish-white precipitate of the hydrated tetroxide is formed, which is dissolved on cautiously adding the alkali: on the addition of a large excess of the precipitant the dark-brown solution deposits potassium hypovanadate, $(V_2O_4)_2K_2O.7H_2O$, in reddish-brown crystalline scales. Ammonia behaves in a similar manner. Ammonium sulphide forms a dark-brown precipitate, soluble in excess. Tincture of galls gives a black liquid, due to the formation of a finely-divided gallo-tannate.

The vanadates are sparingly soluble in water: on the addition of an acid their solutions acquire an orange-red colour, which changes to blue on treatment with oxalic acid or sulphur dioxide. Chromic acid, which is the only other acid forming an orange solution, becomes green on reduction with the same reagents. Vanadic pentoxide may be further distinguished from chromic acid by the formation of a dark-red colour when its solution is agitated with an ethereal solution of hydrogen dioxide.

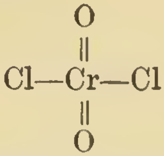
CHAPTER X.

GROUP VI.—HEXAD METALS.

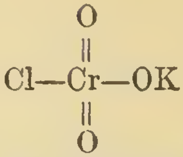
MOLYBDENUM.	CHROMIUM.
TUNGSTEN.	MANGANESE.
URANIUM.	IRON.
	RUTHENIUM.
	OSMIUM.

MOLYBDENUM, tungsten, and uranium, together constitute a well-defined group. The atomic value of tungsten is indicated by its hexchloride, dioxychloride, and trioxide. Molybdenum and uranium form analogous oxychlorides and trioxides but no hexchlorides. Tungsten and molybdenum each form a pentachloride, MCl_5: these compounds may be volatilised unchanged, and afford normal vapour densities. Uranium also appears to form a similar chloride, but its exact molecular weight is unknown, as it cannot be vapourised; from the general analogy of uranium to molybdenum and tungsten its formula is presumably UCl_5. The significance of the existence of these anomalous compounds has been already referred to; they seem to indicate that the elements cannot be rigidly divided into groups of odd and even atomic values. The atomic weight of uranium was formerly assumed to be half the value now adopted: its analogies to tungsten and molybdenum are, however, inexplicable if the lower value be taken. The question of the exact value can only be finally settled by a determination of the specific heat of uranium.

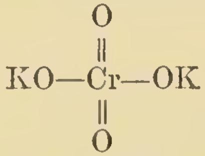
The atomicity of chromium is indicated by the hexfluoride, CrF_6, the chromyl dichloride, CrO_2Cl_2, and the trioxide. The following compounds may be supposed to contain hexadic chromium:—


$$\mathrm{Cl{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}Cl}$$

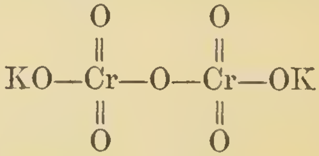
Chromyl Dichloride.


$$\mathrm{Cl{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}OK}$$

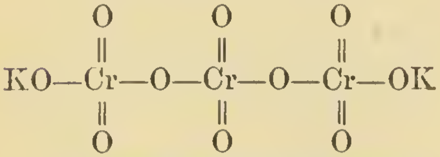
Potassium Chlorochromate.


$$\mathrm{KO{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}OK}$$

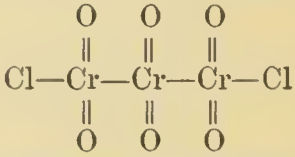
Dipotassium Chromate.


$$\mathrm{KO{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}O{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}OK}$$

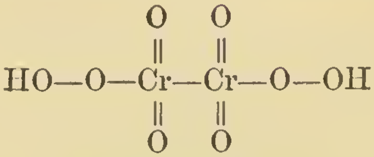
Dipotassium Dichromate.


$$\mathrm{KO{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}O{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}O{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}OK}$$

Dipotassium Trichromate.

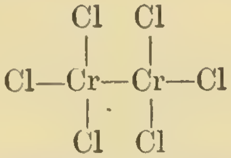

$$\mathrm{Cl{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}Cl}$$

Trichromyl Dichloride.

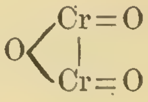

$$\mathrm{HO{-}O{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}}\underset{\overset{\|}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cr}}}\mathrm{{-}O{-}OH}$$

Perchromic Acid.

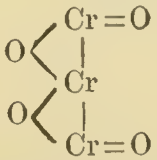
In many of its compounds, however, chromium behaves as a tetrad; as, for example, in chromic chloride, Cr_2Cl_6, in the chromic oxides, Cr_2O_3, Cr_3O_4 and CrO_2, and in the analogous sulphides:


$$\mathrm{Cl{-}}\underset{\overset{|}{\mathrm{Cl}}}{\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{Cr}}}\mathrm{{-}}\underset{\overset{|}{\mathrm{Cl}}}{\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{Cr}}}\mathrm{{-}Cl}$$

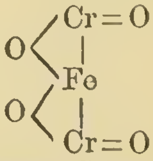
Chromic Chloride.



Dichromic Trioxide.



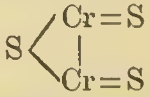
Trichromic Tetroxide.



Chrome Iron-ore.

$O{=}Cr{=}O$

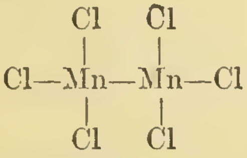
Chromium Dioxide.



Dichromic Trisulphide.

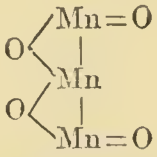
The evidence of the hexadicity of manganese and iron mainly rests upon their analogy to chromium. The manganates are isomorphous with the chromates, and a hexfluoride of manganese is supposed to exist. In many of their combinations these elements, like chromium, are distinctly tetradic.

The following formulæ exhibit the different atomic values of manganese:—

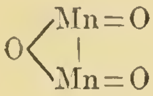


$$\begin{array}{ccccccc} & & \mathrm{Cl} & & \mathrm{Cl} & & \\ & & | & & | & & \\ \mathrm{Cl} & — & \mathrm{Mn} & — & \mathrm{Mn} & — & \mathrm{Cl} \\ & & | & & | & & \\ & & \mathrm{Cl} & & \mathrm{Cl} & & \end{array}$$

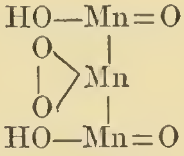
Manganic Chloride.



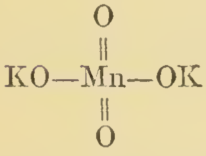
Hausmannite.



Braunite.

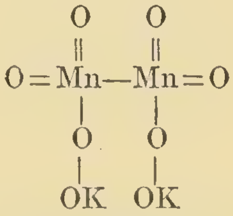


Psilomelane.



$$\begin{array}{ccccc} & & \mathrm{O} & & \\ & & \| & & \\ \mathrm{KO} & — & \mathrm{Mn} & — & \mathrm{OK} \\ & & \| & & \\ & & \mathrm{O} & & \end{array}$$

Dipotassium Manganate.



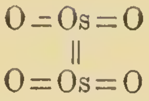
$$\begin{array}{ccccccc} & & \mathrm{O} & & \mathrm{O} & & \\ & & \| & & \| & & \\ \mathrm{O} & = & \mathrm{Mn} & — & \mathrm{Mn} & = & \mathrm{O} \\ & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & \\ & & \mathrm{OK} & & \mathrm{OK} & & \end{array}$$

Dipotassium Permanganate.

The corresponding compounds of iron may be represented by similar formulæ.

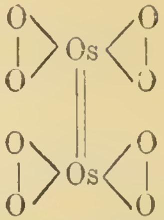
Ruthenium and osmium form tetroxides of the formulæ OsO_4 and RuO_4, or Os_2O_8 and Ru_2O_8: these compounds are interesting from the fact that they are the only tetroxides (octoxides) known. Both metals also form trioxides, which, however, exist only in combination in the rutheniates and osmiates, compounds of the general formulæ M_2RuO_4 and M_2OsO_4.

Many of the derivatives of these metals are apparently best represented on the assumption that ruthenium and osmium are hexads, as represented in the following formulæ;—

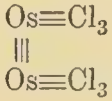


$$\begin{array}{c}\mathrm{O{=}Os{=}O}\\ \|\\ \mathrm{O{=}Os{=}O}\end{array}$$

Osmium Dioxide.

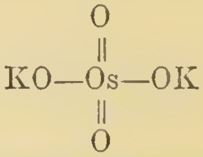


Osmium Tetroxide.



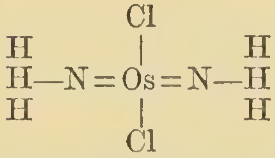
$$\begin{array}{l}\mathrm{Os{\equiv}Cl_3}\\ |||\\ \mathrm{Os{\equiv}Cl_3}\end{array}$$

Osmium Trichloride.



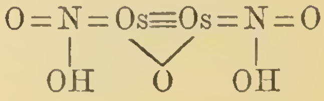
$$\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{KO{-}Os{-}OK}\\ \|\\ \mathrm{O}\end{array}$$

Potassium Osmiate.



$$\begin{array}{lcl}\mathrm{H} & \mathrm{Cl} & \mathrm{H}\\ & | & \\ \mathrm{H{-}N} & \mathrm{{=}Os{=}} & \mathrm{N{-}H}\\ & | & \\ \mathrm{H} & \mathrm{Cl} & \mathrm{H}\end{array}$$

Osmammonium Chloride.



Osmiamic Acid.

The analogous ruthenium compounds may be represented in a similar manner. But, as in the case of the other elements of this group, osmium and ruthenium also appear to behave as tetrads in many of their compounds.

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294. Molybdenum—Symbol Mo; atomic weight 96.—This element was discovered by Scheele in 1778. It is found principally as the sulphide or *molybdenite*, and as lead molybdate or *wulfenite*. The metal is obtained by heating its oxides or certain molybdates with charcoal or potassium cyanide; when fused it has a silvery-white lustre and is exceedingly hard; its specific gravity is about 8·6. At ordinary temperatures it suffers no change on exposure to air, but when heated it is oxidised, acquiring first a yellow and then a blue tarnish. At a high temperature it becomes incandescent and is converted into the trioxide. By fusion with nitre it forms potassium molybdate; it decomposes steam at a high temperature, and is dissolved by chlorine water. Molybdenum alloys readily with other metals: the "bears" or metallic masses occasionally found in the hearths of copper furnaces are often chiefly composed of a molybdide of iron.

295. Molybdenum forms three oxides, Mo_2O_3, MoO_2, and MoO_3. The two latter bodies combine together to form oxides which may be regarded as molybdenum molybdates.

The **sesquioxide** is a black powder which is rapidly oxidised by exposure to air; when hydrated, it dissolves in acids, forming black or dark-purple, and nearly opaque, solutions.

The **dioxide** is formed by reducing the trioxide in hydrogen at a low temperature. As thus prepared it is a reddish-brown powder which resists the action of the strongest acids. It may be obtained in lustrous violet crystals by fusing sodium molybdate with zinc, and treating the mass, when cold, with caustic potash and hydrochloric acid. When strongly heated, both forms of the oxide are converted into the trioxide. The hydrated dioxide, obtained by adding excess of ammonia to a salt of molybdenum, is a brownish-red flocculent precipitate which bears a strong resemblance to ferric hydrate. It is insoluble in potash solution, but dissolves readily in a solution of the acid carbonate of potassium; it is also slightly soluble in water.

The **trioxide** is occasionally found native as *molybdin* or *molybdenum ochre*. It is readily obtained by roasting the native sulphide in air; or by treating lead molybdate with sulphuric acid, filtering, and evaporating the filtrate to dryness after the addition of nitric acid. It is a white powder of specific gravity 3·49; it melts at a red heat, and forms on cooling a straw-coloured crystalline mass. When heated in a stream of air it sublimes and condenses in thin colourless plates. It is but slightly soluble in water; but when a solution of sodium molybdate, mixed with excess of hydrochloric acid, is subjected to dialysis a solution of the true molybdic acid is obtained of a yellow colour and acid reaction, and capable of expelling carbon dioxide from alkaline carbonates. A solution of the acid may also be made by decomposing precipitated barium molybdate by an equivalent quantity of sulphuric acid. On evaporating the solution *in vacuo* molybdic acid is obtained as a transparent bluish-green mass, which parts with its water on heating, and is converted into the trioxide. Molybdic acid combines with bases in many proportions to form salts. The following classes have been described:—

Monomolybdates,	$RO.MoO_3$
Dimolybdates,	$RO.2MoO_3$
$\frac{1}{3}$ Molybdates,	$3RO.7MoO_3$
Trimolybdates,	$RO.3MoO_3$
Tetramolybdates,	$RO.4MoO_3$
Octomolybdates,	$RO.8MoO_3$
Decamolybdates,	$RO.10MoO_3$
Hexdecamolybdates,	$RO.16MoO_3$.

where R signifies 2 atoms of a monad or 1 atom of a dyad metal.

The most important salts are the ammonium molybdates $(NH_4)_2MoO_4$; $(NH_4)_2O.3MoO_3 + H_2O$; and $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}MoO_4$; and lead molybdate, $PbMoO_4$, which occurs native, as *yellow lead ore* or *wulfenite.*

When ammonium molybdate is added to a solution of phosphoric acid, or a tribasic phosphate, a bright-yellow precipitate is formed, usually consisting of $P_2O_5.20MoO_3 + Aq$ (Debray), and termed **phospho-molybdic acid.** The proportion of the molybdic acid is subject to variation, a compound containing only one-fourth of the above quantity of molybdic acid being also known. The formation of this yellow precipitate is occasionally employed as a test for phosphoric acid. Arsenic and silicic acids give similar precipitates; hence the reaction is only applicable to the detection of phosphoric acid in the absence of these compounds.

296. Molybdenum Dichloride, $MoCl_2$ or Mo_2Cl_4, is an amorphous powder of a yellow colour, obtained by heating the metal in chlorine gas. It dissolves in strong hydrochloric acid, and may be obtained from the solution in crystals of the formula $Mo_2Cl_4.3H_2O$.

The **trichloride,** $MoCl_3$ or Mo_2Cl_6, is a crystalline red powder, formed by passing the tetrachloride mixed with hydrogen through a red-hot tube. Heated in a stream of carbon dioxide it is resolved into the di- and tetra-chlorides.

$$Mo_2Cl_6 = MoCl_2 + MoCl_4.$$

The **tetrachloride,** $MoCl_4$, is also formed by heating molybdenum in an excess of chlorine: it is a brownish-black crystalline solid, somewhat resembling iodine. It is highly deliquescent, and dissolves in water with a considerable rise of temperature.

The **pentachloride**, $MoCl_5$, is a black crystalline mass which melts at a low temperature, and may be sublimed unchanged in an atmosphere of chlorine. It gives a brown-red vapour. When heated in the air it forms the dioxydichloride MoO_2Cl_2: it is a bright-yellow crystalline body, and is decomposed by water. Several other oxychlorides of molybdenum are known. Similar combinations with bromine have been described.

297. **Molybdenum Disulphide**, MoS_2, occurs native as *molybdenite* or *molybdenum glance*: the mineral has a leaden-grey colour and high metallic lustre. It may be formed artificially as a black lustrous powder by igniting the trioxide with sulphur. It is readily converted into the trioxide by roasting in air.

The **trisulphide**, MoS_3, is formed by passing sulphuretted hydrogen through a solution of an alkaline molybdate and adding an acid. It is a dark-brown powder which dissolves in alkalies and alkaline monosulphides and sulphydrates, forming solutions containing alkaline **sulphomolybdates**, M_2MoS_4. On boiling potassium sulphomolybdate with molybdenum trisulphide, sulphuretted hydrogen is evolved, and a precipitate is formed from which water extracts **potassium persulphomolybdate** as a red amorphous salt, consisting of $K_2MoS_5 = K_2S.MoS_4$. Similar compounds have been formed with the other alkalies and with the alkaline earths.

Compounds of molybdenum impart to borax in the inner flame a dark-brown colour: in the outer flame the bead becomes yellow whilst hot and colourless when cold. To microcosmic salt they give a green colour in the inner flame.

Molybdous salts in solution give the brownish-black molybdous sulphide, soluble in ammonium sulphydrate. The fixed alkalies give the dark-brown hydrate soluble in ammonium carbonate.

Molybdic salts afford reddish-brown solutions which become blue by oxidation. The formation of this blue colour may be used as a means of recognising molybdenum. The substance suspected to contain this element is heated with a few drops of concentrated sulphuric acid upon platinum-foil. When cold, the mass (which should not be dry) is breathed upon; it becomes blue if molybdenum be present, owing to the formation of a sulphate which acquires this colour at a low temperature, and at a certain stage of dilution.

Molybdic acid, in solution as a molybdate, is readily detected by the formation of hydrated molybdenum trisulphide when the liquid is treated with sulphuretted hydrogen and hydrochloric acid. Stannous chloride forms a bluish-green precipitate, soluble in hydrochloric acid, with the production of a green solution which changes to blue on the further addition of the tin chloride.

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298. **Tungsten**—Symbol W (Wolfram); atomic weight 184.—This element was discovered by d'Elhujar in 1781. It is never found free in nature : its principal native compounds are *wolfram*, a tungstate of iron and manganese occurring in Cornwall and Saxony; calcium tungstate or *scheelite*, a mineral found principally in Saxony and Bohemia; and lead tungstate which occurs in Bohemia, Carinthia, and Chili. The metal is obtained by reducing the trioxide in hydrogen, or by passing the vapour of tungstic chloride mixed with hydrogen through a red-hot tube, or by passing the vapour of the chloride over heated sodium. It is an infusible steel-grey crystalline powder of specific gravity 18·0; when heated in the air it burns, forming tungstic oxide. When mixed with other metals it forms exceedingly hard, infusible alloys.

Tungsten unites with oxygen in three proportions to form the oxides WO_2, WO_3, and W_2O_5. The dioxide WO_2 or W_2O_4, is obtained as a brown powder by reducing the trioxide at a low red heat; or in copper-coloured scales, by treating the trioxide with zinc and hydrochloric acid. A **sodium tungstite**, $Na_2O.W_2O_4$, is formed by saturating fused sodium tungstate with the trioxide, and heating the mass in hydrogen gas. On washing out the undecomposed sodium tungstate with water, the tungstite is obtained in metallic-looking scales closely resembling gold.

299. **Tungstic Trioxide**, WO_3, occurs in nature as *tungstic ochre*, a yellowish mineral, found in Cumberland and in the United States. It is readily obtained from native calcium tungstate, and from wolfram by digestion with hydrochloric acid. It is a light-yellow powder, which may be obtained crystallised by strong ignition with borax, or by heating a mixture of sodium tungstate and carbonate in hydrochloric acid gas. It becomes denser when strongly heated; its specific gravity varies from 5·27 to 7·14, according to the mode of its preparation. It is insoluble in water and in acids. Its colour changes to green on exposure to light; when strongly heated it becomes dark-orange. It is readily reduced on heating with hydrogen or charcoal, yielding first the dioxide, and ultimately the metal. When heated in ammonia gas it yields **tungsten-nitretamidioxide**, $3WN_2.2W(NH_2).2WO_3$, a black powder not attacked by acids or alkalies.

Tungstic trioxide dissolves in aqueous solutions of the alkalies, and forms salts termed **tungstates**, from which **tungstic acid**, H_2WO_4, is obtained as a yellow powder by addition of a dilute acid to the heated liquid. If the solution of the alkaline tungstate be cold and dilute, the addition of the mineral acid precipitates **tungstic dihydrate** as a white gelatinous mass of the composition $H_2WO_4.H_2O$. This substance occurs native as *meymacite*, and is formed by the decomposition of scheelite. Two modifications of the acid exist, viz., the ordinary tungstic acid, which is insoluble in water but soluble in concentrated acids, and which forms insoluble salts with all bases, except the alkalies; and **metatungstic acid**, which dissolves in water, and forms soluble salts with the majority of the basic oxides. Metatungstic acid is obtained by decomposing a concentrated solution of barium metatungstate, BaW_4O_{13}, by sulphuric acid. On concentrating the filtered solution a thick syrupy liquid is obtained, which deposits quadratic octahedrons of hydrated metatungstic acid, $H_2O.WO_3.7H_2O$. The acid is very soluble in water; it has a strong bitter taste, and dissolves zinc and iron with evolution of hydrogen and formation of the blue oxide of tungsten.

Ordinary tungstic acid forms acid and neutral salts: the general formula of the latter is M_2WO_4; that of the former, according to Laurent and Marignac, is $5M_2O.12WO_3.xH_2O$. The most important salt is the sodium tungstate, $Na_2WO_4.2H_2O$, which is occasionally used as a mordant, and for rendering fabrics non-inflammable. Calcium tungstate, $CaWO_4$, occurs native as *scheelite* or *tungsten* (Swedish for heavy stone; in allusion to the high specific gravity, viz., 6·1, of the mineral); it may be obtained artificially in crystals by fusing wolfram with calcium chloride. Ferroso-manganous tungstate, $(Fe:Mn)WO_4$, is found in nature as *wolfram*, associated with tin ores and galena, in Cornwall, Cumberland, and in various parts of Scotland, Saxony, and Bohemia. Lead tungstate, $PbWO_4$, is also found native as the mineral *scheeletine*, isomorphous with lead molybdate. None of the acid salts occurs native.

The metatungstates possess the generic formula $M_2WO_4.3WO_3$. The alkaline metatungstates are formed by boiling tungstic acid with solutions of the ordinary alkaline tungstates; the other metatungstates may be obtained from the alkaline salts by double decomposition. They are generally soluble in water, and hence give no precipitates with salts of the heavy metals, with the exception of those of lead and mercury. Their acidulated solutions give no reaction with potassium ferrocyanide, whereas ordinary tungstates afford a brown flocculent precipitate after addition of hydrochloric acid. On treatment with zinc and hydrochloric acid they become at first blue and eventually purple; ordinary tungstic acid under similar circumstances gives a brown colour.

A solution of tungstic acid in concentrated hydrochloric acid affords a remarkable succession of colours on the gradual addition of small fragments of zinc. At first a fine blue is obtained, which gradually changes to violet and purple, then becomes crimson, then green, and eventually orange-brown. On adding ether to the liquid when crimson it changes to blue, and is rapidly decolourised. Metatungstic acid gives a similar series of colours, except that no crimson is produced. If the solution of the tungstate be mixed with an alkaline sulphocyanate and dilute hydrochloric acid, and then treated with zinc, a deep green solution is obtained, which changes to purple, and ultimately to a very deep amethystine colour.

A solution of metatungstic acid under similar conditions acquires a blue colour, which gradually changes to brown.

A solution of metatungstic acid is occasionally used as a test for alkaloids, with the solutions of which it gives highly insoluble precipitates. A convenient way of preparing the test consists in adding phosphoric acid in excess to a solution of ordinary sodium tungstate. The solution thus obtained will detect 1 part of strychnine or quinine in 200,000 parts of water.

When gelatinous silica is added to a hot solution of acid sodium tungstate, it is dissolved with formation of an alkaline **silicotungstate.** The solution gives, with mercurous nitrate, a heavy yellow precipitate of **mercurous silicotungstate,** $Hg_8SiW_{12}O_{42}$, which, by treatment with hydrochloric acid, forms **silicotungstic acid,** $SiO_2.12WO_3.4H_2O$. It is a strong acid, which decomposes carbonates and forms crystallisable salts, for the most part soluble in water, termed **silicotungstates.** An isomeric form of the acid is known and may be termed **tungsto-silicic acid**; its salts are distinguished from the corresponding silicotungstates by differences in crystalline form, amount of water of crystallization, and degree of solubility. An acid, termed **silicodecatungstic acid,** of the composition $SiO_2 10WO_3.4H_2O$, is known. It gives rise to a highly-soluble series of salts, characterised by the formation of a white precipitate with mercurous nitrate.

300. Tungsten unites with chlorine in four proportions to form the compounds WCl_6, WCl_5, WCl_4, and WCl_2, or W_2Cl_4: it also forms two oxychlorides of the composition $WOCl_4$ and WO_2Cl_2.

Tungsten Hexchloride, WCl_6, is formed by the direct union of its elements, or by heating the sulphide or the oxide mixed with charcoal, in chlorine gas. It forms dark-violet crystals; it melts at 275° and boils at 346°. When pure it is permanent in the air, but rapidly deliquesces and is decomposed if containing a trace of the oxychloride. It is decomposed by water and alcohol, but is readily dissolved by carbon disulphide without change. At 350° it gives a normal vapour density, but at a higher temperature it suffers dissociation. When heated with ammonium chloride it forms **tungsten nitride**, WN_2, and **tungsten nitretamide**, $2WN_2W(NH_2)_2$.

Tungsten Pentachloride, WCl_5, is obtained in the form of black, shining, highly deliquescent needles by treating the preceding compound with hydrogen at a low temperature. It melts at 248° and boils at 275°·6.

Tungsten Tetrachloride, WCl_4, and **Dichloride**, W_2Cl_4, are formed by still further abstracting the chlorine from the hexchloride. The former is a crystalline, greyish-brown, highly-deliquescent powder: the latter is a grey non-crystalline solid.

Tungsten Monoxychloride, $WOCl_4$, is prepared by passing the vapour of the hex- or penta-chloride, mixed with chlorine, over heated tungstic trioxide. It forms fine ruby-red crystals, which melt at 210° and volatilise at 227°·5 without decomposition.

Tungsten Dioxydichloride, WO_2Cl_2, is obtained by passing chlorine over heated tungsten dioxide. It forms a bright-yellow powder, which volatilises at 267°.

Tungsten hexbromide, contrary to the statement of Riche, does not exist: the highest known bromide being the **pentabromide**, which is a dark-coloured lustrous compound, gradually decomposing into WBr_4 (?). On treating it with hydrogen the **dibromide**, W_2Br_4, is obtained. Oxybromides, corresponding to the oxychlorides, are known, and are obtained in a similar manner.

301. Tungsten Disulphide, WS_2, is formed by heating its elements together; by passing vapour of carbon disulphide over ignited tungstic oxide; or by fusing acid potassium tungstate with sulphur and treating the fused mass with water. It forms black needle-shaped crystals, which oxidise when heated in air.

Tungsten Trisulphide, WS_3, is a dark-blue or black powder, formed by adding hydrochloric acid to a solution of tungstic trioxide in ammonium sulphide. It combines with the alkaline sulphides, forming **sulphotungstates** possessing the general formula M_2WS_4, corresponding to the neutral tungstates.

Two combinations of phosphorus and tungsten are known, viz., W_3P_4 and W_4P_2. The latter is obtained crystallised in lustrous hexagonal prisms of a steel-grey colour, by heating a mixture of tungstic and phosphoric oxides to a high temperature in a crucible lined with charcoal.

Compounds of tungsten give with microcosmic salt in the inner flame, a pale blue colour, which becomes blood-red in presence of an iron salt, but changes to a dark-blue on the addition of a stannous salt.

The reactions of the soluble compounds of tungsten have already been given (see Tungstic Acid). The formation of the colours on the addition of zinc and hydrochloric acid is especially characteristic. Sodium hyposulphite, Na_2SO_2, formed by the action of zinc upon solution of acid sodium sulphite, produces an intense blue colour, by means of which as little as 1 part of tungstic acid in 10,000 parts of solution may be detected (Mallet).

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302. Uranium—Symbol U; atomic weight 240.—The existence of this element was first indicated by Klaproth in 1789. Its most abundant source is *pitchblende*, an impure uranoso-uranic oxide, $UO_2.2UO_3$, found principally in Saxony and Cornwall. It occurs also as a carbonate; as *uranium-vitriol;* as a phosphate in *uranium-mica;* and combined with niobium, tantalum, and titanium in the rare minerals *samarskite* and *euxenite*. The metal is obtained by heating uranous chloride with sodium or potassium as a black powder, or as a reguline mass. To prepare it, a mixture of 75 grams of uranium tetrachloride, 150 grams dry potassium chloride, and 50 grams of sodium in small pieces, is placed, in alternate layers, in a porcelain crucible, and the whole is covered with a layer of potassium chloride. The porcelain crucible is placed within a plumbago crucible, the intervening space being filled with charcoal powder, and is heated in a wind furnace. The reaction occurs at a red heat, and with great regularity; the uranium is found in the regulus. The specific gravity of the metal is 18·33. It slowly tarnishes on exposure to air, and becomes incandescent when heated, forming a dark-green oxide; when thrown into chlorine it takes fire, forming uranous chloride, UCl_4.

303. Uranous Oxide, UO_2, is a brown powder formed by heating the uranoso-uranic oxide, or the uranic oxalate in hydrogen gas. On solution in acids it forms green-coloured uranous salts.

Uranoso-uranic Oxide, U_3O_8 or $UO_2.2UO_3$, is found native as *pitchblende*, and may be obtained artificially by heating the metal or the other oxides in air. It is a dark-green powder but little acted upon by dilute acids. It is used for producing a black colour on porcelain.

Uranic Oxide, UO_3, is a yellowish powder, formed by igniting the nitrate. It may be obtained hydrated, forming the compounds $UO_3.4H_2O$ and $UO_3.2H_2O$: the water cannot be completely expelled without decomposition of the oxide. Uranic oxide unites with basic metallic oxides, forming a series of yellow insoluble salts, termed **uranates**, which possess the general composition $M_2U_2O_7$, analogous to the acid chromates. The best known members are the sodium and ammonium salts, which are used to some extent as pigments, and for colouring glass. The mineral *trögerite* has the composition $3UO_3.As_2O_5.12H_2O$; *uranosphœrite* has the formula $Bi_2O_3.UO_3.H_2O$.

On mixing solutions of uranic nitrate, $UO_2N_2O_6$, and hydrogen dioxide a light-yellow precipitate of the formula $UO_4.2H_2O$ is obtained. This substance appears to be a compound of uranic oxide, UO_3, and a **peroxide**, UO_6; thus $UO_6.2UO_3.6H_2O$ (Fairley).

304. Uranium Pentachloride, UCl_5, is made by passing chlorine over a moderately-heated mixture of charcoal and any of the oxides of uranium: it forms long needle-shaped crystals, which are green by reflected and ruby-red by transmitted light. It is also obtained as a pale-brown light amorphous powder. The difference in appearance depends upon the rapidity of formation. Both modifications rapidly deliquesce to yellowish-green liquids, and are decomposed by water with evolution of heat. The chloride cannot be volatilised without decomposition.

Uranous Chloride, UCl_4, is formed by the direct union of its elements; by heating uranous oxide in hydrochloric acid gas; or, together with the pentachloride, by passing chlorine over a strongly-heated mixture of the oxide and charcoal. The chloride forms a dark-green crystalline mass of a strong metallic lustre: on heating, it volatilises, giving a red vapour. It is extremely deliquescent, and dissolves in water with a considerable rise of temperature. On boiling, the solution is decomposed, and uranous hydrate is precipitated. When heated in hydrogen gas it forms the **subchloride**, UCl_3, a dark-brown powder which dissolves in water forming a purple solution.

Uranyl Chloride, or **Uranium Dioxydichloride**, UO_2Cl_2, is a yellow, crystalline, volatile solid, made by heating uranous oxide in chlorine gas. It is soluble in water, and combines with alkaline chlorides to form double salts. Corresponding compounds of bromine, iodine, and fluorine, are known. The **fluoxyuranates** have the general formula MUO_2F_5, corresponding to the fluoxymolybdates and fluoxytungstates.

305. Uranous Sulphide, US_2, may be formed by the direct union of the metal and sulphur, or by heating uranous chloride in a stream of sulphuretted hydrogen. It is a greyish-black powder which becomes crystalline on ignition out of contact with air.

Uranous Oxysulphide, $UO_2.2US_2$, is formed by heating pitchblende to redness in vapour of carbon disulphide.

Uranic Oxysulphide, or **Uranyl Sulphide**, UO_2S (?), is said to be obtained by adding ammonium sulphide to a solution of **uranic nitrate**, $UO_22NO_3.6H_2O$.

Uranium compounds impart a greenish-yellow colour to borax or microcosmic salt in the outer flame; in the inner flame the colour changes to bright-green.

Uranous salts afford green solutions from which ammonium sulphide throws down the black uranous sulphide. Caustic potash or soda forms the reddish-brown uranous hydrate. Ammonium carbonate produces a green precipitate soluble in excess. Uranic salts form yellow solutions, which give a black precipitate of uranic sulphide with ammonium sulphide: in the case of the nitrate, uranyl sulphide appears to be formed. Potash produces a yellow precipitate of potassium uranate, $K_2U_2O_7$. Potassium ferrocyanide affords a reddish-brown precipitate.

306. Chromium—Symbol Cr; atomic weight 52·1.—The principal naturally-occurring compound of this element is *chrome ironstone* ($FeOCr_2O_3$), which occurs massive in Silesia, Hungary, Norway, Siberia, Asia Minor, and North America. It is isomorphous with magnetic oxide of iron; it has a brownish-black colour and sub-metallic lustre. Other native compounds of chromium are *chrome ochre*, a yellowish-green earthy deposit, found in the Shetland Isles and in various parts of France and Sweden; and in *crocoisite* and *melanochroïte*, lead chromates, of an orange or yellow colour, found in Brazil and in the Ural. A chromate of lead and copper termed *vauquelinite*, after the French chemist Vauquelin, who discovered chromium in 1797, is occasionally found associated with crocoisite. The colour of the emerald, of green serpentine, olivin, etc., is due to the presence of small quantities of chromium. The metal is obtained by strong ignition of the sesquioxide with charcoal, or by heating chromic chloride with zinc or potassium. It has a steel-grey colour, and is exceedingly hard; its specific gravity is about 6.

307. Chromium Monoxide, CrO, is obtained as a hydrate by the action of potash solution on the dichloride. When moist it is yellow, but on drying its colour changes to brown; it is exceedingly unstable, and when ignited is transformed into the sesquioxide with the evolution of hydrogen.

Chromic Oxide or Chromium Sesquioxide, Cr_2O_3, is formed by the oxidation of the metal or the monoxide in air, or by the decomposition of certain chromates, and of chromic anhydride. Thus, if mercurous chromate be heated in a covered porcelain crucible, oxygen and mercury are expelled, and pure chromic oxide, of a fine green colour, is obtained. This substance is also obtained as a bulky amorphous powder, of a dull-green colour, by igniting the acid ammonium chromate. It may be procured in rhombohedral crystals, of a dark-green colour and as hard as corundum, by passing the vapour of chromyl dichloride, CrO_2Cl_2, through a red-hot tube. It may be obtained as a bluish-green hydrate by adding caustic soda or potash to a solution of a green or violet chromium salt; it dissolves in excess of solution of potash in the cold, but on boiling it is reprecipitated; ammonia produces the same precipitate, which has either a greyish-green or greyish-blue colour, according as the chromic salt from which it is derived is green or violet. Both precipitates dissolve in excess of cold ammonia with a purple colour. The state of hydration of the precipitates appears to vary with the temperature and degree of concentration of the solutions.

Chromium sesquioxide is used as a pigment, under the name of *chrome* or *emerald green.* It is chiefly employed in porcelain painting, and in the manufacture of glass and enamel. A very brilliant colour is obtained by igniting a mixture of boric oxide and acid potassium chromate, and treating the fused mass with water. Another form of chrome green may be obtained by heating a mixture of calcium phosphate and potassium bichromate with sugar.

Chromium Dioxide or **Chromium Chromate,** CrO_2 or $Cr_2O_3.CrO_3$, is a dark-brown hygroscopic powder obtained by partial reduction of the trioxide or the chromic nitrate. It is most easily prepared by passing nitric oxide into dilute solutions of potassium dichromate.

Chromium Trioxide, CrO_3, may be formed by the action of sulphuric acid upon a chromate. The barium or lead chromates, when boiled with this acid, yield chromic acid and insoluble lead or barium sulphates. It is also readily prepared by the addition of sulphuric acid to a solution of acid potassium chromate; at a certain stage of concentration the sparingly-soluble potassium sulphate crystallises, and on further evaporation the trioxide separates out in scarlet crystals. It deliquesces on exposure to air and is readily soluble in water; a saturated solution contains about 62 per cent. of the oxide. Chromium trioxide has a specific gravity of 2·788; it melts at 190°(?), and decomposes at 250°, forming first the dioxide and eventually the sesquioxide. It is one of the most powerful oxidising agents known. It sets fire to warm absolute alcohol, 'and becomes incandescent in a mixture of alcohol and bisulphide of carbon vapours. It is, however, soluble in ether without decomposition. Ammonia gas is rapidly oxidised to water and nitrogen with formation of the sesquioxide, the trioxide becoming red-hot from the energy of the reaction. A moderately-diluted aqueous solution of the oxide acts more gradually, and is frequently employed in the laboratory as an oxidising agent.

The trioxide is also reduced by the action of sulphur dioxide, sulphuretted hydrogen, and nascent hydrogen.

The chromates are an important class of salts, and several of them are used to a considerable extent in the arts. They are generally isomorphous with the corresponding sulphates. The best known of the series are the potassium, lead, and zinc chromates, which are used in calico printing, and in the manufacture of pigments.

Potassium Bichromate, $K_2Cr_2O_7$, is made on the large scale by roasting a mixture of finely-powdered chrome ironstone with potassium carbonate and lime in a reverberatory furnace. The addition of the lime is necessary to prevent the mass fusing, as in that case the heavy chrome-ore would sink to the bottom, and would be very slowly acted upon. The reaction is as follows:—

$$2FeOCr_2O_3 + 3K_2CO_3 + CaO + 7O = 3K_2CrO_4 + CaCrO_4 + Fe_2O_3 + 3CO_2.$$

The roasted mass is lixiviated with water, and treated with potassium sulphate, in order to decompose the calcium chromate:

$$CaCrO_4 + K_2SO_4 = CaSO_4 + K_2CrO_4.$$

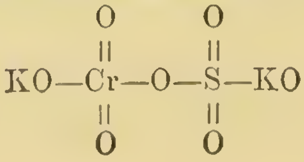
The solution is allowed to clarify by standing, and is mixed with sulphuric acid:

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O.$$

The greater portion of the bichromate rapidly separates out and is purified by recrystallization. The mother liquors containing the potassium sulphate are employed in the treatment of fresh roasted ore.

Potassium bichromate forms large bright garnet-red triclinic crystals. It melts below a red heat and crystallises on solidifying. At a very high temperature it evolves oxygen and forms a mixture of the normal chromate and the sesquioxide. 100 parts of water at 0° dissolve 4·6 parts of the salt; at 10°, 7·4 parts; at 20°, 12·4 parts; and at 100°, 94·1 parts: a saturated solution boils at 103·4°.

A **potassium sulphato-chromate,** $K_2SO_4.CrO_3$ or



$$\mathrm{KO—}\overset{\displaystyle O \atop \|}{\underset{\displaystyle \| \atop O}{\mathrm{Cr}}}\mathrm{—O—}\overset{\displaystyle O \atop \|}{\underset{\displaystyle \| \atop O}{\mathrm{S}}}\mathrm{—KO}$$

i.e., potassium bichromate in which a portion of the chromyl (CrO_2) is replaced by sulphuryl (SO_2) may be prepared by mixing sulphuric acid with potassium bichromate. Indeed, the two radicles form a considerable number of analogous derivatives as will be evident from the following formulæ:—

$$CrO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$$

Chromyl Dichloride.

$$SO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$$

Sulphuryl Dichloride.

$$CrO_2\left\{\begin{matrix}OK\\OK\end{matrix}\right.$$

Potassium Monochromate.

$$SO_2\left\{\begin{matrix}OK\\OK\end{matrix}\right.$$

Potassium Monosulphate.

$$\begin{matrix}CrO_2\left\{\begin{matrix}OK\\ \\ \end{matrix}\right.\\ \quad O\\ CrO_2\left\{\begin{matrix}OK\\ \\ \end{matrix}\right.\end{matrix}$$

Potassium Anhydrochromate.
(Potassium Bichromate.)

$$\begin{matrix}SO_2\left\{\begin{matrix}OK\\ \\ \end{matrix}\right.\\ \quad O\\ SO_2\left\{\begin{matrix}OK\\ \\ \end{matrix}\right.\end{matrix}$$

Potassium Anhydrosulphate.

$$CrO_2\left\{\begin{matrix}OK\\NH_2\end{matrix}\right.$$

Potassium Amidochromate.

$$SO_2\left\{\begin{matrix}OK\\NH_2\end{matrix}\right.$$

Potassium Amidosulphate.

$$\begin{matrix}CrO_2\left\{\begin{matrix}Cl\\O\\Ba\end{matrix}\right.\\ CrO_2\left\{\begin{matrix}O\\Cl\end{matrix}\right.\end{matrix}$$

Barium Chlorochromate.

$$\begin{matrix}SO_2\left\{\begin{matrix}Cl\\O\end{matrix}\right.\\ SO_2\left\{\begin{matrix}Ba\\O\\Cl\end{matrix}\right.\end{matrix}$$

Barium Chlorosulphate.

The **neutral** or **normal potassium chromate**, K_2CrO_4 or $CrO_2\left\{\begin{matrix}OK\\OK\end{matrix}\right.$, is a pale-yellow salt isomorphous with potassium sulphate, readily soluble in water, with the formation of a bright-yellow solution.

When the dichromate is heated with strong nitric acid it forms a salt of the composition $CrO_2\left\{\begin{matrix}OK\\NO_2\end{matrix}\right.\cdot CrO_3$. Treated with chromic acid the dichromate yields a **terchromate** of the composition $K_2Cr_3O_{10}$. With strong hydrochloric acid it forms a **chlorochromate of potassium**, $CrO_2\left\{\begin{matrix}OK\\Cl\end{matrix}\right.$, crystallising in long needles. Similar compounds are formed by the chlorides of calcium, barium, and magnesium.

On treating the chlorochromate with ammonia gas, ammonium chloride is formed, together with a salt of the composition $\left\{\begin{matrix} CrO_2OK \\ CrO_2 \\ CrO_2OK \end{matrix}\right.$. A corresponding ammonium salt is also known.

By the action of ammonia gas upon the chlorochromate in presence of ether, **potassium amidochromate**, $CrO_2\left\{\begin{matrix} OK \\ NH_2 \end{matrix}\right.$, is produced.

Normal Lead Chromate, $PbCrO_4$, is formed as a bright-yellow powder, known in the arts as *chrome yellow*, by the addition of a soluble salt of lead to a solution of an alkaline chromate. In calico printing the colour is formed directly on the fabric by first steeping it in a solution of a salt of lead and then in that of a chromate. A **diplumbic chromate**, $2PbO.CrO_3$, of a deep-orange or red colour, and known in commerce as *chrome-red*, is formed by fusing the normal chromate with nitre. This colour may be produced on calico by steeping the fabric dyed with chrome yellow in boiling lime-water.

Normal lead chromate is occasionally used instead of cupric oxide in organic analysis. It is decomposed by boiling with strong nitric acid with the formation of lead nitrate and chromic acid, but on the addition of water the lead chromate is reproduced.

308. **Chromous Chloride**, $CrCl_2$ or Cr_2Cl_4, is a white crystalline substance obtained by passing hydrogen over gently-heated chromic chloride, or by heating a mixture of chromic oxide and charcoal in chlorine gas. It is soluble in water, and forms a blue solution which becomes green on exposure to air. Ammonia gives a light-blue precipitate which changes to green in contact with air. If sal-ammoniac be added to the liquid and then ammonia, the blue colour gradually changes to red. Chromous chloride is a powerful reducing agent; it precipitates gold from its solutions, forms cuprous oxide with cupric compounds, and calomel with corrosive sublimate.

Chromic Chloride, Cr_2Cl_6, is obtained in shining scales of a beautiful purple or peach-blossom colour by heating a mixture of the sesquioxide and charcoal in a rapid stream of chlorine. When pure it is absolutely insoluble in cold water, but if it contains even a trace of chromous chloride, which is apt to be formed if the chlorine has not been present in sufficient excess, it dissolves immediately, forming a green solution. The purple-coloured chromic chloride is a body of great stability: it may be boiled with any of the strong mineral acids without decomposition. Hydrogen reduces it on heating to chromous chloride, and if the heat be sufficiently intense the metal is formed. It is oxidised to sesquioxide on heating to redness in the air, chlorine being evolved. With hydrogen phosphide it forms **chromium phosphide**, CrP, a black crystalline powder; ignited in ammonia, it yields the **nitride** as a brown powder of unknown composition.

Chromic hydrate is soluble in hydrochloric acid and forms a green solution of chromic chloride, which, on evaporation in a vacuum, yields green crystals of the composition $Cr_2Cl_6.2H_2O$. On heating in hydrochloric acid or in chlorine to 250° this compound parts with its water and turns purple, but the salt is still soluble in water; if, however, the temperature be raised until the chloride sublimes, it becomes insoluble. If the green solution of chromic chloride be evaporated to dryness, and the dried mass heated, a number of oxychlorides are formed, the composition of which varies with the temperature of their formation.

Chromyl Dichloride, CrO_2Cl_2, is a dark-red fuming liquid of specific gravity 1·92, boiling at 116°·8 under a pressure of 733 mm. It is easily formed by heating a mixture of potassium chromate and common salt with sulphuric acid. It is decomposed by water, forming chromic and hydrochloric acids. When it is heated in a sealed tube, it loses chlorine, and is transformed into **trichromyl dichloride**, $(CrO_2)_3Cl_2$ or

$$\left\{\begin{array}{l}CrO_2Cl\\CrO_2\\CrO_2Cl\end{array}\right.$$

, a black amorphous deliquescent powder which ignites in hydrogen, forming chromic oxide, hydrochloric acid, and water. This substance may also be made by the action of iodine upon chromyl dichloride, or by heating potassium chlorochromate with sulphuric acid.

309. A **fluoride of chromium**, CrF_6(?), is formed by heating a mixture of lead chromate and fluor-spar with sulphuric acid in a leaden retort. It is a very volatile,

strongly fuming, dark-red liquid, which is decomposed by water with formation of chromic and hydrofluoric acids. It is not improbable that this substance contains oxygen, and is analogous to the chromyl dichloride.

310. Ammonium sulphide added to solutions of chromium salts gives a precipitate of the hydrate only. The **sulphide** corresponding to this oxide is obtained by igniting the sesquioxide in vapour of carbon disulphide or sulphuretted hydrogen. It is a dark-grey crystalline powder which is converted into chromic oxide on heating in air. A dark-brown powder said to have the composition Cr_4S_3 is obtained by reducing chromic sulphate in hydrogen. It ignites on exposure to air, forming chromic oxide and sulphur dioxide.

311. Chromic Sulphate, $Cr_2(SO_4)_3$, is obtained by dissolving chromic hydrate in sulphuric acid. When perfectly free from water the salt is red, but on hydration it becomes violet or green. By mixing the solution with ammonium or potassium sulphate, **chromium alums** are obtained of a splendid ruby or purple colour.

312. Ammoniacal Chromium Compounds.—Chromic hydrate dissolves in ammoniacal salts containing free ammonia, and the solution after a time deposits a compound of the composition $Cr_2O_3.2NH_3$. On treatment with acids this substance is converted into **roseochromammonia,** $Cr_2O_3.8NH_3$, a base which gives crystalline salts of a wine-red colour. The **tetramine-chromic chloride,** the chloride of the base, has the composition $Cr_2Cl_6.8NH_3.2H_2O$. Similar compounds have been obtained with bromine and iodine.

Compounds of chromium colour borax green both in the inner and outer flame of the Bunsen lamp. Fused with potassium carbonate and nitrate, they produce yellow potassium chromate, which, after the addition of acetic acid, forms, with silver nitrate, the reddish-brown silver chromate, and with lead acetate, the yellow lead chromate.

Chromic salts afford green or violet solutions, which yield the hydrate on the addition of caustic alkalies or ammonium sulphydrate.

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313. Manganese—Symbol Mn; atomic weight 54·0.—

Compounds of manganese are very widely distributed, although the element itself is never found free in nature. One of the most commonly occurring of these compounds is the black oxide, MnO_2, a substance formerly regarded as an ore of iron, and termed *magnesia nigra,* from its resemblance to the loadstone. About the middle of the last century this mineral was shown to contain an element distinct from iron; a supposition confirmed in 1774 by the extraction from it of the metal manganese by Gahn. Manganese may be obtained by reducing the dioxide or the carbonate with charcoal or soot, at a high temperature. A carbide of the metal is thus formed, corresponding to cast-iron, which may be refined by reheating with manganese carbonate. As thus obtained the metal has a greyish-white colour and a fine-grained structure; it is very brittle, and rapidly oxidises when exposed to air. Its specific gravity is about 8. It fuses only at the highest temperature of a blast furnace, and is rapidly attacked by dilute mineral acids, with evolution of hydrogen.

Manganese readily unites with many metals, but the alloys, with the exception of that with iron, are not of much importance.

The following oxides of manganese are known :—

Manganous oxide,...	MnO
Trimanganic tetroxide,...	Mn_3O_4
Manganic oxide,...	Mn_2O_3
Manganese dioxide,...	MnO_2

The oxides corresponding to the manganic and permanganic acids have not been isolated.

The **Monoxide**, MnO, is a greenish powder, obtained by mixing saturated solutions of potassium permanganate and oxalic acid, adding acetic acid, drying, and heating in hydrogen; by igniting the carbonate or oxalate in hydrogen; or by fusing a mixture of manganous chloride and sodium carbonate containing a small quantity of sal-ammoniac, and exhausting the mass with water. By heating it to bright redness, in a mixture of hydrogen and hydrochloric acid gas, it may be obtained crystallised in transparent octahedrons of an emerald-green colour. **Manganous hydrate** is obtained as a white flocculent precipitate by adding caustic potash to a solution of a manganous salt.

It rapidly oxidises on exposure to air, and turns brown from the formation of **manganic hydrate.**

Trimanganic Tetroxide, or **Manganoso-Manganic Oxide,** Mn_3O_4, occurs native as *hausmannite,* and is readily obtained by strongly heating the preceding oxide, or the nitrate or carbonate, in contact with air; or by intense ignition of the higher oxides. The artificial oxide is a reddish-brown powder, which temporarily darkens on heating. It is sparingly soluble in the cold concentrated mineral acids without decomposition, but definite combinations have not been obtained. When heated with sulphuric acid it evolves oxygen, and manganous sulphate is formed; hot hydrochloric acid yields chlorine and manganous chloride.

The **Sesquioxide,** or **Manganic Oxide,** Mn_2O_3, is found in nature as *braunite.* It may be obtained artificially by heating the nitrate or the dioxide to redness; at a higher temperature the manganoso-manganic oxide is alone formed. The nature of the product is, moreover, modified by the tension of the oxygen in the atmosphere in which the oxide is heated. On heating with hydrochloric and sulphuric acids it behaves like the preceding oxide. The corresponding **hydrate,** $Mn_2H_2O_4$, is found native in *manganite,* and may be prepared by the gradual oxidation of the manganous hydrate. It forms very unstable salts, a few only of which have been prepared: the phosphate appears to be the only one which can be obtained perfectly stable. The oxide enters into the composition of certain double salts of greater stability. An alum of the composition $Mn_2K_2(SO_4)_4 24H_2O$ occurs in violet octohedrons on the shores of the Great Salt Lake.

The **Peroxide** or **Dioxide,** MnO_2, is the most valuable ore of manganese; it has long been used for "correcting" the green or brown tints of glass; hence its mineralogical name of *pyrolusite* (πυρ, fire; λυειν, to wash).* It may be obtained artificially by heating manganous carbonate to a temperature of about 260°, in contact with air. This fact is made use of on the large scale in recovering the manganese from the solutions of manganous chloride formed by the action of hydrochloric acid upon the dioxide in the manufacture of bleaching powder (Vol. I., p. 274). The liquor from the stills is treated with milk of lime to precipitate the iron, alumina, and silica originally contained in the manganese ore, and is afterwards mixed with finely-divided chalk and heated in iron boilers under pressure, when the following reaction occurs :—

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* The French call it *savon des verriers.*

$$MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2.$$

The washed manganous carbonate is then slowly heated in trays in a furnace, resembling the annealing oven of glass-works: it gradually loses carbon dioxide, and is converted into a mixture of the dioxide and protoxide.

In the Weldon recovery process the still-liquor is mixed with excess of lime, whereby a precipitate of manganous hydrate is obtained, which is afterwards oxidised by blowing air through it. A certain quantity of a compound of calcium oxide and manganic oxide is also formed, which, however, is decomposed on treatment with hydrochloric acid when the mixture is returned to the still, in accordance with the equation—

$$MnO_2.CaO + 6HCl = MnCl_2 + CaCl_2 + Cl_2 + 3H_2O,$$

When strongly heated the dioxide parts with a portion of its oxygen, and is converted into Mn_2O_3 or Mn_3O_4, according to the temperature employed. Heated with strong sulphuric acid it gradually gives off half its oxygen and yields manganous sulphate. Heated with hydrochloric acid, or with a mixture of sulphuric acid and common salt, chlorine is evolved: these reactions are employed in the preparation of this gas for manufacturing purposes (see Vol. I., p. 266). The dioxide unites with water in various proportions, and several of its hydrates occur native.

Psilomelane, *varvicite*, and *wad*, are naturally-occurring mixtures of manganese oxides. *Cupreous manganese* is a mixture of oxides of manganese and oxide of copper, and, occasionally, of oxide of cobalt.

Chalcophanite (χαλκος, brass; φαινος, I appear), in allusion to the change on heating, is a crystalline compound of hydrated oxides of zinc and manganese.

314. Manganic Acid, MnH_2O_4.—This acid is known only in combination. When a mixture of manganese dioxide, potassium chlorate, and caustic potash, is ignited at a low red heat, and the cooled mass digested with cold water, a deep-green solution of potassium manganate is formed which gradually becomes red owing to the absorption of oxygen and the production of potassium permanganate. By evaporating the green solution *in vacuo* over sulphuric acid, dark-green crystals of the manganate, MnK_2O_4, may be obtained. Barium and sodium manganates have also been prepared. All the salts are very unstable, being decomposed even by carbonic acid.

Permanganic Acid, $Mn_2H_2O_8$, or $Mn_2O_6(OH)_2$.—A solution of a manganate very rapidly becomes red on boiling, and is converted into a permanganate. The best known permanganate is the potassium salt. It is prepared by mixing 4 parts of the finely-powdered dioxide with 3½ parts of potassium chlorate, and adding to the mixture 5 parts of caustic potash dissolved in the minimum quantity of water. The dried mixture is heated until the potassium chlorate is decomposed, and the sintered mass extracted with boiling water. The solution is allowed to clarify by standing, decanted, rapidly concentrated by boiling, poured off from any precipitated peroxide, and set aside to crystallise. Potassium permanganate, $K_2Mn_2O_8$, separates out in dark reddish-purple crystals, which are isomorphous with those of potassium perchlorate. It is soluble in about 16 parts of water at ordinary temperatures, and forms a deep-purple coloured solution. This solution is largely used in quantitative chemical analysis by reason of the ease with which it parts with its oxygen. For the same reason it is employed as a deodoriser and disinfectant. The free acid, $H_2Mn_2O_8$, is obtained as a viscid shining liquid of a greenish-black colour by warming the potassium salt with sulphuric acid diluted with a small quantity of water. It is decomposed when rapidly heated, but when gently warmed it volatilises in violet vapours with but slight decomposition. It decomposes in contact with organic matter, igniting alcohol and other inflammable liquids, occasionally with explosion.

315. **Manganous Chloride**, $MnCl_2$, is readily prepared by heating the dioxide with hydrochloric acid: it is thus obtained in the manufacture of chlorine. When the pure dioxide is used, the solution yields pink and highly-deliquescent crystals

of the composition $MnCl_2.4H_2O$. On heating in an atmosphere incapable of acting upon it, it parts with its water of crystallization, and fuses to a clear colourless liquid. The salt dissolves in alcohol, yielding a green solution, and combines with the alkaline chlorides to form double salts.

Manganic Chloride, $MnCl_4$, is not known in an isolated state, but is supposed to be contained in the brown solution formed by adding the dioxide to cold concentrated hydrochloric acid, or by passing hydrochloric acid gas into a mixture of the dioxide and ether. It gives a bright-green solution which readily evolves chlorine. It is probably formed in the manufacture of chlorine from manganese dioxide and hydrochloric acid: the reaction between these substances, in all probability, occurs in the following stages :—

$$(1)\ MnO_2 + 4HCl = MnCl_4 + 2H_2O$$
$$(2)\ MnCl_4 = MnCl_2 + Cl_2.$$

Manganese Hexachloride, $MnCl_6$(?), is supposed to be formed when a mixture of potassium permanganate, sulphuric acid, and common salt is gently warmed. Dark coloured vapours pass over which may be condensed in a freezing mixture to a greenish-brown liquid. It is possible that this compound may be an oxychloride analogous to the chromyl dichloride.

316. Manganous Sulphide, MnS, is formed by igniting the dioxide with sulphur, or by heating manganic hydrate in the vapour of carbon bisulphide. It occurs native, as *manganese blende.* As a hydrate, it may be formed by passing sulphuretted hydrogen into a solution of manganous acetate, or by the action of an alkaline sulphide on any manganous salt. As thus obtained it is a flesh-coloured powder which rapidly darkens on exposure to air. It is readily soluble in acids; when heated with ammonium sulphide in a sealed tube it becomes green, and is converted into the anhydrous sulphide.

317. Manganous Sulphate, $MnSO_4$, is prepared on the large scale for use in calico printing by igniting the dioxide with powdered coal, and dissolving out the manganous oxide by means of sulphuric acid. It is also formed by heating the dioxide in sulphuric acid, evaporating to dryness, and strongly igniting the mass to decompose any iron sulphate which may be present. On treatment with water manganous sulphate is dissolved. At ordinary temperatures the solution deposits crystals which are isomorphous with those of cupric sulphate, and contain, like that salt, 5 molecules of water. When crystallised below 6° C., the salt contains 7 molecules of water, and has the same form as ferrous sulphate. Both hydrates effloresce in dry air, and at 18° or 20° contain only 4 molecules of water. A solution of the salt evaporated at this temperature yields the tetrahydrated sulphate, isomorphous with the corresponding ferrous salt. Manganous sulphate forms double salts with the alkaline sulphates: the potassium compound has the composition $MnK(SO_4)_2.4H_2O$ when crystallised at ordinary temperatures, and $MnK_2(SO_4)_2.2H_2O$, when deposited at 40° to 50°. Manganous sulphate is occasionally found native, associated with ferrous and zinc sulphates.

Manganic Sulphate, $Mn_2(SO_4)_3$ or $Mn_2(SO_4)_4$ (?), is an unstable compound, formed by triturating the dioxide with strong sulphuric acid, heating the thin paste to about 140°, placing the deep-green mass on a plate of pumice to absorb the excess of sulphuric acid, repeatedly triturating with fresh portions of strong nitric acid, and finally drying at 130°. Manganic sulphate is a dark-green amorphous powder, which deliquesces on exposure to moist air, forming a violet liquid, quickly becoming turbid from the formation of manganic hydrate.

318. Manganous Carbonate, $MnCO_3$, occurs naturally, constituting the mineral *diallogite* or *manganese spar*. It is found associated with the carbonates of iron, calcium, and magnesium, and is isomorphous with calcite. It may be prepared artificially by heating manganous chloride or sulphate with sodium carbonate. It is slightly pink in colour, but becomes brown on ignition in air, owing to the formation of trimanganic tetroxide.

Manganese compounds give a violet or amethystine colour to borax in the outer flame. When fused with sodium carbonate and nitre on platinum-foil, they form the green sodium manganate.

Manganous salts have a pale-pink tint; their solutions give the flesh-coloured hydrated sulphide on the addition of ammonium sulphydrate. Caustic potash forms the hydrate. Ammonia gives no precipitate in presence of excess of ammoniacal salts. On boiling solutions of manganese, free from chlorine, with red-lead and nitric acid, they acquire a purple colour from the formation of permanganic acid.

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319. **Iron**—Symbol Fe (Ferrum); atomic weight 56.—Although iron is now the most abundant and important of the metals, man's acquaintance with it is subsequent to his knowledge of copper, tin, and certain of the noble metals, a fact which is accounted for when we remember that the extraction of iron depends upon metallurgical processes which were, in all probability, unknown in very early times. According to Xenophon, iron ores were first smelted by the Chalubes, a people dwelling in the neighbouring of the Black Sea: hence the word *chalups* (χαγυψ), denoting steel, and hence, too, our modern word *chalybeate* applied to water containing iron. To the alchemist iron was, of course, well known, and was designated by the symbol of Mars, ♂. Metallic iron, apparently of terrestrial origin, is occasionally found associated with platinum. The huge masses of native iron, one block of which was calculated to weigh at least 20,000 kilograms, discovered by Nordenskiöld at Ovifak, in Greenland, are supposed by Daubrée to be of terrestrial origin, and to be formed from basaltic rocks, ejected from great depths. Andrews has shown that finely-divided metallic iron is present in many basalts. Large masses of the metal, sometimes nearly pure, but more frequently alloyed with nickel, cobalt, phosphorus, etc., are met with in various parts of the world; these are unquestionably derived from extra-terrestrial sources. The general composition of these bodies may be seen from the following analysis of a mass of meteoric iron found in Virginia, and analysed by J. W. Mallet (*Sill. Am. J.* [3] ii. 200)—

Iron.	Nickel.	Cobalt.	Copper.	Tin.	Manganese.
88·706	10·163	0·396	·003	·002	trace
Phosphorus.	**Sulphur.**	**Chlorine.**	**Carbon.**	**Silica.**	**Total.**
0·341	·019	·003	0·172	·067	99·872

When heated *in vacuo*, this iron evolved more than three times its volume of gas, consisting of

Hydrogen.	Carbon monoxide.	Carbon dioxide.	Nitrogen.	Total.
35·83	38·33	9·75	16·09	100

The gases evolved on heating various meteorites are very similar in character: they differ mainly in the relative proportion of the constituents. The gases obtained from a number of meteorites have been examined by A. W. Wright, who has shown that their composition is dependent upon the temperature of ignition; thus in the case of a meteorite found in Tennessee—

	Hydrogen.	Carbon monoxide.	Carbon dioxide.	Nitrogen.
At 500°,......	41·51	38·45	18·34	1·70
Red heat,....	44·76	45·75	7·76	1·73

The diminished quantity of carbon dioxide at the higher temperature is probably due to its action on the heated metal. Meteoric iron is seldom homogeneous: it usually contains, disseminated throughout its mass, grains and crystals of various substances, such as *Schreibersite* (Fe_4Ni_2P: Meunier), *Troilite* (FeS: Rammelsberg; $(Fe.Ni)_7S_8$: Meunier), which give rise to the development of peculiar markings, known as *Widmannstatt's figures*, when the iron is treated with hydrochloric or nitric acid, or fused potash.

It has been supposed that in early times meteorites were used as sources of iron, a supposition which seems to derive its chief support from the fact that savages are occasionally found to employ such iron for the manufacture of knives, etc.; forgings of meteoric iron are, however, generally very deficient in strength and tenacity, properties which are not wanting in many articles of ancient iron which have come down to us.

Iron, in a state of combination, is exceedingly widely diffused. Nearly every rock contains it in greater or less quantity; it exists, generally as carbonate, sometimes as chloride, more rarely as sulphate, in nearly all natural waters; and it occurs in the tissues and juices of most animal and vegetable organisms.

The principal ores of the metal are the oxides and carbonates: the sulphides, although very abundant, cannot be used for the manufacture of good iron, apparently from the impossibility of removing the last traces of sulphur, which exercises an injurious effect upon the character of the metal.

The following are the chief varieties of iron ore, in the order of their comparative richness :—

Magnetic ore or *Magnetite.*—This variety is mainly composed of triferric tetroxide, Fe_3O_4, and contains, when pure, nearly 72 per cent. of iron. It is met with chiefly in the northern parts of Europe, in Siberia, and North America, although it is also found to some extent in Southern Europe, and in Mexico. Probably the oldest workings in the world, viz., those at Traversella in Piedmont, are among deposits of magnetic ore. The largest deposit of iron ore in Europe consists of magnetite, and is found in Southern Lapland, but from the inaccessible character of the district it has been but little worked. The celebrated Dannemora iron is made from magnetic ore, found in the southern part of Sweden. Magnetite very rarely occurs in this country in sufficient quantity to make its extraction profitable.

Magnetite is found both massive and crystallised in forms derived from the regular system, generally in octahedrons or rhombic dodecahedrons. It has a black colour, with a tinge of brown or even green. It is very hard, and its density is about 5·2. As its name signifies it is highly magnetic : it is the chief constituent of the loadstone.

Hæmatite, one of the most abundant and widely diffused of iron ores, consists mainly of the sesquioxide, Fe_2O_3, and contains, when pure, about 70 per cent. of the metal. It occurs in a great many different forms, some of which have received special names, as *specular ore* or *iron glance*, a hard brilliant variety, crystallising in rhombohedral plates, and found in the island of Elba, and in South America ; *micaceous ore* occurring in loosely-coherent plates somewhat resembling graphite ; and *kidney ore* found in dark-red botryoidal masses in Cumberland.

Hæmatite ores are found to some extent in Sweden, and are largely worked in Canada. The principal deposits in Europe occur in Saxony, and, in this country, in Cumberland and North Lancashire. They are also met with in Cornwall, in Staffordshire, and in South Wales. The specular ore of Elba has been worked for more than 2000 years, and was the source from which the Romans derived their main supplies of the metal.

Ilmenite or *titaniferous ore* is found in crystals resembling those of hæmatite: it may be regarded as derived from ferric oxide by the replacement of a portion of the iron oxide by oxide of titanium. It has a dead-black colour and a brown streak, whereas the colour of hæmatite varies from dark-red to blue-grey, and its streak is invariably red.

Occasionally the sesquioxide occurs crystallised with a molecule of water, in forms derived from a rhombic prism, giving rise to several varieties which are classed together under the name of *göthite:* when pure this compound contains about 63 per cent. of iron and 10·5 of water. The colour varies from an ochreous-yellow to a dark reddish-brown; it is frequently met with in fibrous aggregations, the surfaces of which exhibit a remarkable velvety lustre.

Brown ore is a variable mixture of hydrated oxides: its normal composition is usually stated to be $2Fe_2O_3.3H_2O$, which requires about 60 per cent. of iron and 14·5 per cent. of water. The chief deposits of this ore in this country are found in Northamptonshire, in the Forest of Dean, and in Glamorganshire. It also occurs in France, and in Luxembourg, and affords a considerable proportion of the iron smelted on the Continent. The *bog* and *lake ores* of North Germany and Scandinavia may be classed as brown ores. According to Ehrenberg they are of infusorial origin, being produced by diatomaceæ secreting iron from water, and depositing it as sesquioxide in their siliceous coverings. In Sweden and Norway considerable quantities of these ores are obtained by dredging from the bottoms of lakes, upon which the oxide lies in detached concretionary masses. They usually contain notable quantities of phosphates which detract from the quality of the iron which they yield.

Spathic ore consists mainly of ferrous carbonate, $FeCO_3$, and contains, when pure, about 48¼ per cent. of iron. It frequently occurs in well-defined crystals, derived from the rhombohedral system. When pure it is perfectly white, but more frequently possesses a grey or yellowish-brown colour, due to partial oxidation. Spathic ores sometimes contain considerable quantities of the isomorphous manganous carbonate, which increases their value for special purposes, as for the manufacture of steel. The *clayband* ores or *clay ironstones* of this country are mainly ferrous carbonates associated with clay; the *blackband* ore, which is chiefly met with in Scotland, contains, in addition, more or less carbonaceous matter.

Spathic ores in England occur chiefly in Durham, Cornwall, Devon, and Somersetshire. On the Continent they are met with along the Rhine, in Styria, Carinthia, and Thuringia.

The *clay ironstone*, although poor in iron as compared with hæmatite and magnetite, is the most important ore in this country: it furnishes nearly two-thirds of the iron produced in Great Britain. It is found in the shales of the coal measures in Staffordshire, Shropshire, Yorkshire, Derbyshire, Denbigh, and South Wales, either in beds or in nodules of a light greyish-yellow tint, which become brown by exposure to air.

The table on the following page gives the composition of several of these varieties of iron ore.

Analysis and Valuation of Iron Ores.—In order to form an opinion of the value of an iron ore, it is necessary not only to determine the amount of metallic iron which it will yield, but also to ascertain the nature of the accompanying earthy matters and the amount of the substances present which are likely to exert an influence on the character of the metal produced. In order to analyse it, the weighed quantity (say about 10 grams) of the finely-powdered ore is digested with concentrated hydrochloric acid and a little nitric acid, and the solution is evaporated to dryness: the dried mass is moistened with hydrochloric acid, treated with hot water, and the *silica* and insoluble earthy matter filtered off and weighed. By boiling the weighed mixture with a solution of sodium carbonate, the *silica* is dissolved; on again weighing the residue after washing and drying, the proportions of the silica and insoluble matter (gangue) are determined. It is sometimes required to ascertain the nature of the residue, whether, for example, it is mainly composed of clay or fusible silicates: for this purpose, recourse must be had to the general methods employed in silicate analyses.

	MAGNETIC.	HÆMATITE.	B HÆMATITE	BOG ORE.	SPATHIC ORE	CLAY IRON-STONE.	BLACKBAND.
	Dannemora.	Whitehaven.	Forest of Dean.	Sweden.	Durham.	Low Moor.	Scotland.
Iron peroxide, ...	28·42	95·16	90·05	67·50	...	0·61	45·84
,, protoxide, ...	62·06	...	...	...	49·47	36·14	0·20
Manganese ,, ...	...	0·24	0·08	1·45	2·42	1·38	...
Lime, ...	...	0·07	0·06	0·47	3·47	2·70	1·90
Magnesia, ...	1·44	...	0·20	0·23	3·15	2·05	5·90
Alumina, ...	...	...	...	4·18	...	0·52	2·53
Sulphur, ...	0·07	...	...	...	0·08	0·10	...
Carbonic acid, ...	...	...	...	...	37·71	26·57	33·63
Water, etc., ...	...	...	9·22	17·81	...	1·77	1·86
Silica, ...	7·60	...	...	7·81	4·93	...	7·83
Phosphoric acid, ...	...	...	0·09	0·18	...	0·34	...
Insoluble matter, ...	...	5·68	1·07	...	...	27·67	...
	99·59	101·15	100·77	99·63	101·23	99·85	99·69
Metallic iron, ...	65·6	66·6	63·04	47·32	38·56	29·12	28·40

The solution obtained after filtering off the silica is diluted to a definite volume, say 500 c.c., and is well mixed by shaking. An aliquot portion, say 100 c.c., of the solution is withdrawn, evaporated nearly to dryness in a porcelain dish, to expel the greater portion of the free acid, diluted with water and mixed with two or three drops of barium chloride solution. After standing for a few hours, the precipitated barium sulphate is filtered off and weighed. Its weight, divided by 0·137, gives the amount of *sulphur* in the aliquot portion of the ore. To a second portion of 100 c.c. of the solution a small quantity of a solution of ammonium molybdate in nitric acid is added, and the mixture is heated for a few hours to a temperature of about 40°, when, if phosphorus be present, a bright-yellow precipitate consisting of a variable mixture of a compound of molybdic and phosphoric acids with ammonia is formed; if its quantity be small, it is collected on a filter, previously weighed, and after washing and drying, its weight is determined. According to Seligsohn, the average composition of the precipitate, dried at 100°, may be thus stated:—

Molybdic acid,	90·744
Phosphoric acid,	3·142
Ammonium oxide,	3·570
Water,	2·544
	100·000

If its quantity be large, it is better to dissolve the precipitate in ammonia and add magnesium chloride. The magnesium ammonium phosphate which is formed is collected, ignited, and weighed, as magnesium pyrophosphate. On dividing its weight by 0·279, the amount of phosphorus in the portion of the ore which is being analysed is found.

A third portion of 100 c.c. of the solution is boiled with a small quantity of nitric acid, ammonium carbonate solution is added little by little until the fluid is nearly neutral, and then ammonium acetate in excess: the liquid is then boiled for some time and filtered. The precipitate contains the ferric oxide, alumina, and phosphoric acid. It is redissolved in dilute hydrochloric acid, mixed with solutions of tartaric acid, ammonium chloride and sulphide, and filtered after standing. The filtrate is mixed with sodium carbonate and nitre evaporated to dryness and ignited, redissolved in dilute hydrochloric acid, and the *alumina* and *aluminium phosphate* precipitated by adding ammonium chloride and ammonia. The weight of the precipitate, less that of the phosphoric acid, gives the weight of the *alumina.*

The filtrate from the precipitated acetate contains the manganese, alkalies, and alkaline earths. A few drops of bromine are added to it; the solution is heated in a flask to about 40° and tightly corked. The *manganese* separates out as the dioxide : it is filtered off, ignited, and weighed as trimanganic tetroxide, Mn_3O_4. The filtrate is concentrated by evaporation, mixed with ammonia and ammonium oxalate, and the precipitated calcium oxalate collected, washed, ignited, and weighed as *lime.* The filtrate from the calcium oxalate precipitate, containing the magnesia and alkalies, is evaporated to dryness, ignited to expel ammoniacal salts, the residue dissolved in a small quantity of water mixed with about 1 gram of oxalic acid, the solution again evaporated to dryness and ignited: alkaline carbonates and magnesia are thus obtained. On heating with water, the *magnesia* remains undissolved, and may be filtered off and weighed. The alkalies in the solution are converted into chlorides by the addition of a few drops of hydrochloric acid evaporated to dryness and weighed. The proportion of the potassium chloride in the alkaline chlorides may be determined by means of platinum tetrachloride (see potassium), the difference is the amount of the sodium chloride.

The quantity of *moisture* in the ore is determined by igniting a few grams of it in a tube attached to a weighed calcium chloride tube : the increase in the weight of the calcium chloride tube gives the amount of water present. The amount of *carbon dioxide* is most accurately estimated by treating a weighed portion of the finely-powdered ore with dilute hydrochloric acid, and absorbing the evolved carbon dioxide in tubes filled with soda-lime.

The determination of the quantity of *iron* in the ore is readily effected by volumetric analysis. Two processes are in common use, known respectively as the "Bichromate" and "Permanganate" methods. The former method depends upon the fact that when a solution of potassium bichromate is added to a solution of a ferrous salt, containing free hydrochloric acid, the iron is converted into a ferric salt at the expense of the oxygen of the bichromate:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

It is evident from the equation that 294·4 parts of potassium bichromate will convert 336 parts of iron, as ferrous salt, to the state of ferric salt. It will be also clear that if we have a solution of potassium bichromate of known strength, and a method of ascertaining when the whole of the iron has been changed to the ferric compound, we shall be able to determine from the volume of the bichromate solution needed how much iron is present in the solution. The solution of iron to be tested is placed in a flask, and a few fragments of zinc are thrown into it: hydrogen is evolved, which reduces the iron to the lower state of oxidation. The solution of the bichromate is then added, drop by drop, from a measuring vessel, termed a burette, until a drop of the iron solution added to a small drop of very dilute potassium ferricyanide solution placed on a white plate no longer gives a blue colouration (fig. 161). The volume of the bichromate solution needed is then read off on the burette, and from the known value of the solution the amount of iron is readily calculated. A solution of convenient strength is made by dissolving 4·907 grams of the potassium bichromate in a litre of water: 1 cb. c. of this solution is equivalent to ·0056 gram of iron.

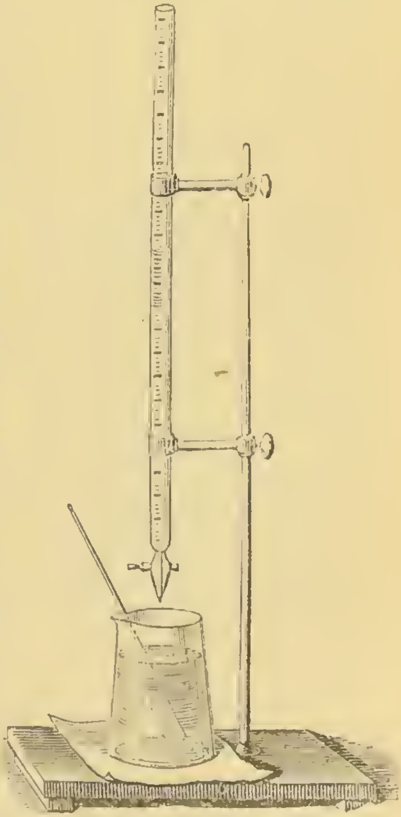

Fig. 161.

The permanganate process is based upon the circumstance that when a solution of this salt is dropped into a solution of iron (best in sulphuric acid), the iron is peroxidised at the expense of the oxygen of the potassium permanganate, which is thereby converted into a mixture of potassium sulphate and manganous sulphate. So long as any ferrous salt remains in solution the colour of the permanganate is almost instantly discharged: the final point of the reaction is therefore ascertained by the permanence of the pink tinge of the liquid. The reaction may be thus expressed:

$$10FeSO_4 + K_2Mn_2O_8 + 8SO_4H_2 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

As potassium permanganate is a somewhat unstable salt, the oxidising value of its solution is best ascertained by preliminary experiments made with solutions containing a known amount of iron.

The majority of these processes are equally applicable to the determination of the same constituents in manufactured iron.

Manufacture of Iron.—A description of the methods of extracting iron belongs more particularly to the province of Metallurgy; these are fully detailed in the treatise on that subject published in this series. It is only necessary, therefore, to refer to these processes in so far as they involve chemical changes.

In this country iron ores are subjected to but little mechanical treatment before being smelted, but on the Continent, where comparatively poor argillaceous ores are frequently employed, dressing and washing are resorted to, in order to remove sand and clay. Ores are occasionally "weathered" by exposing them in heaps to the action of the air and moisture: the sulphides are thus partially converted into soluble sulphates which are removed by the rain. In the case of the clay iron ore from the coal measures the weathering is attended with a further advantage, inasmuch as it causes the disintegration of the associated shale. Care must be taken, especially in the case of spathic ores containing much lime, not to carry the exposure too far, otherwise the mass is apt to fall to powder when calcined or when treated in the blast furnace.

Calcining.—It is generally necessary to subject the ores to a preliminary roasting before they are treated in the smelting furnace, in order to expel water and carbon dioxide;

of course, in the case of such ores as red hæmatite and magnetite, which are practically free from these substances, this operation is not requisite. The process of roasting is not only beneficial in expelling volatile ingredients and in thus concentrating the metallic oxide; it also facilitates the smelting operations by rendering the roasted fragments more porous, whereby the reducing gases penetrate the mass more readily. Calcination also expels the greater part of the sulphur, and thoroughly peroxidises the iron; the complete conversion of the oxide to ferric oxide diminishes the tendency of the iron to unite with silica to form a fusible slag. The calcination is effected either in piles or clamps in the open air; between walls; or in specially-constructed kilns or furnaces. Certain ores, as the blackband ironstones, contain so large a quantity of carbonaceous matter that it is unnecessary to use additional fuel in the roasting, and accordingly such ores are most conveniently treated in clamps; in other cases, and more especially where economy of fuel and uniformity in the composition of the product are important considerations, it is preferable to roast in kilns. Fig. 162 represents Gjers' calcining kiln which is in general use in the Cleveland district.

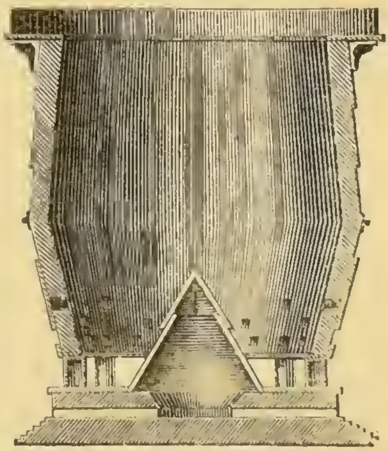

Fig. 162.

A quantity of ignited coal is placed at the bottom of the shaft, and a mixture of ore and fuel is added from the top from time to time. As the mass is roasted it is withdrawn at the bottom, being directed outwards by the internal cone. The roasting is occasionally accomplished by means of the waste gases from the blast furnace. The loss of weight suffered by the ores in this process varies greatly. The average qualities of argillaceous ore lose about one-fourth, blackband ores about one-third, and brown hæmatites about one-seventh of their weight.

Smelting.—Oxides of iron, when heated, are readily reduced by carbonaceous matter, or by the action of hydrogen, carbon monoxide, and gaseous hydrocarbons. If the ores to be operated upon consisted of pure oxides, the extraction of iron would, theoretically speaking, be a very simple operation. The actual process is complicated by the circumstance that the oxides are almost invariably accompanied by more or less siliceous matter, so that when the iron becomes partially reduced it combines as protoxide with the silica to form a fusible slag. It is necessary, therefore, to arrange matters so as to prevent this combination of the silica with the iron oxide, and at the same time to prevent the accumulation of it and the other earthy matters within the furnace. This may be effected in two ways: either by mixing ores, the earthy material of which will together form a proper flux, or by adding aluminous or calcareous minerals, free from iron, to the ore. The substance most generally added is calcium carbonate, in the form of limestone; the lime unites with the silica and alumina of the clay to form a readily-fusible double silicate of calcium and aluminium. The choice of limestone is by no means an unimportant matter: a highly fossiliferous limestone is objectionable from the quantity of phosphates it usually contains, and a dolomitic limestone diminishes the fusibility of the slag. In Cumberland and North Lancashire, where the rich red hæmatites are smelted, it is often necessary to add an aluminous flux, either as shale from the coal measures, or in the form of certain varieties of brown hæmatite containing a large quantity of alumina.

The economical production of iron depends in great measure upon the formation of the most readily-fusible slag in sufficient quantity, with the smallest addition of extraneous materials, *i.e.*, substances free from iron. The fusibility of the slag depends upon the relative amounts of lime, alumina, and silica which it contains: the most fusible mixture is stated to be composed of 56 per cent. of silica, 30 of lime, and 14 of alumina, corresponding to the formula $Al_2O_3.3CaO.5SiO_2$.

Usually, however, the amounts of lime and alumina are considerably larger, and that of the silica much less. The following analyses of slag will show the nature of the ingredients, and the extreme variability of the product:—

	Dowlais.	Wigan.	Cleveland.
Silica, ...	43·07	31·46	27·68
Alumina, ...	14·85	8·50	22·28
Lime, ...	28·92	52·00	40·12
Ferrous oxide, ...	2·53	0·76	0·80
Manganous oxide,.......	1·37	2·38	0·20
Magnesia, ...	5·87	1·38	7·27
Calcium sulphide,.......	1·90	2·96	2·00
Phosphoric acid, ...	...	...	...
Alkalies,...................	1·84	...	...
	100·35	99·44	100·35

The composition and physical characters of the slag, together with the amount produced, vary greatly with the working conditions of the furnace. Slags are of nearly all colours: in the manufacture of grey iron they are usually white; but with an increased charge in the furnace, and at a comparatively low temperature, they become almost black from the increased quantity of iron present. They have usually a vitreous lustre, but when containing a large quantity of alumina they possess an appearance resembling that of porcelain. A stony slag, disintegrating on exposure to air, is indicative of excess of lime: such slags are formed in the production of highly-carburetted iron, and are comparatively infusible. As a general rule, it may be stated that an infusible slag is accompanied by the production of grey iron; if very fusible the iron will be white. The formation of grey iron under these conditions is accounted for by the circumstance that the reduced metallic particles are unable to coalesce, owing to the refractory nature of the slag with which they are intermingled; they are thus exposed to conditions favourable to the accumulation of carbon and silicon, which latter element determines in some measure the greyness of the iron, although not to the same extent as the carbon. Many proposals have been made to utilise the slag produced in such enormous quantity; at present it is mainly used as "road metal," but is capable of being made into bricks and hydraulic cement.

The Blast Furnace.—Fig. 163 represents a vertical section of a modern blast furnace. Its typical form may be regarded as that of two truncated hollow cones, placed base to base: the widest portion of the furnace, or the boshes (*bauch*, German), being at the place of junction of the two cones. The newer forms of blast furnace differ from those of older construction in the avoidance of corners and angles in the interior. The furnace thus assumes a shape somewhat resembling that of an ordinary soda-water bottle without the neck and pointed end. The extreme upper part of the furnace is termed the *tunnel-head:* at its mouth the gases produced by the reaction between the materials in the furnace burn, if allowed to escape into the air. In the figure the *throat* of the furnace is represented as being closed by a cup and cone arrangement: the gases pass through an opening, *k*, into a pipe, *l*, which leads thence to the stoves employed in heating the blast, in the manner described below. The charges of ore, limestone and fuel, are thrown from trucks or barrows running along the gallery or charging plate, *m*. The manner in which the materials are brought on to the charging plate depends upon the natural situation of the furnace. Sometimes the furnaces are built upon the sides or at the bottom of declivities, in order that advantage may be

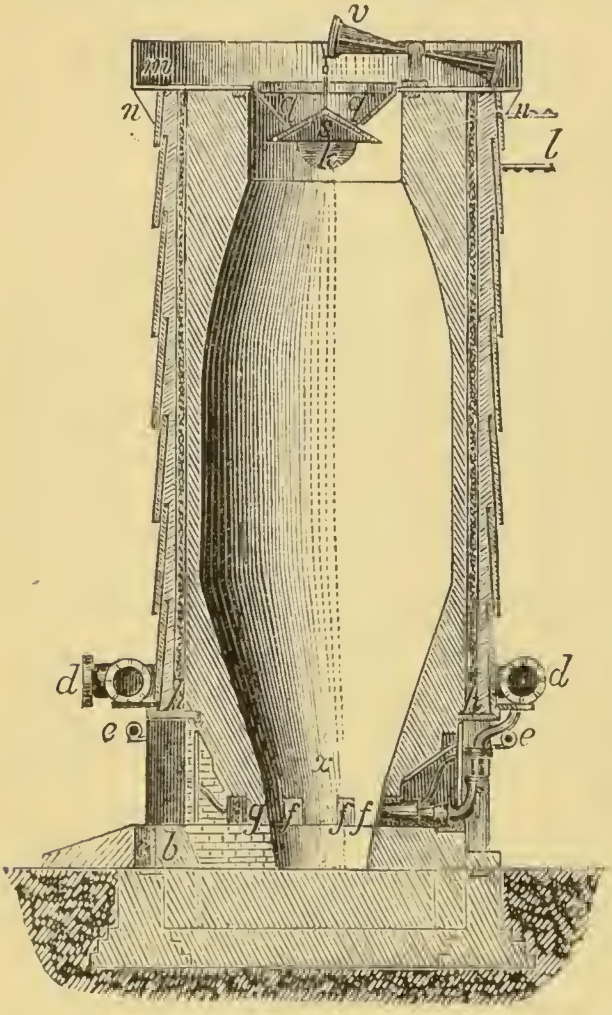

Fig. 163.

taken of the rising ground to deliver the charges directly at the mouth of the furnace; more frequently, however, the materials are raised by hydraulic or pneumatic lifts. From the "throat" of the furnace the diameter of the shaft or "stack" begins to increase gradually, until the boshes are reached, when it commences to decrease, and is narrowed at the bottom, on which the molten products collect. The walls of the sloping hearth are perforated, so as to contain the pipes or "twyers" (*ff*), which are supplied with air from the blowing engines. As the temperature of the furnace at this point is exceedingly high, it is necessary to protect the twyers from melting by surrounding them with water. Fig. 164 shows one form of twyer in detail: the arrows indicate the direction in which the water flows; the projection and inclination of the twyer within the furnace are regulated by the screw and ball and socket joint *a*. The flanged elbow pipe fits on to the main supplying the blast; at *b* is a small opening which can be closed with a plate of glass, through which a view of the interior of the hearth can be obtained. The number of the twyers and method of arranging them varies in different districts, as many as sixteen being sometimes used, as in Rachette's furnace: three, however, is the usual number, two being placed at the sides and the third at the back. The pressure of the blast varies with the character of the fuel used, the weight of the materials in the furnace, and the nature of the iron desired: in England it is usually from 3 to 5 lbs. on the square inch, but in the American anthracite furnaces it amounts to nearly half an atmosphere, whilst in the charcoal furnaces of Sweden it is only a fraction of a pound. In some of the larger iron-works the blowing engines are capable of delivering enormous volumes of air, as much as 50,000

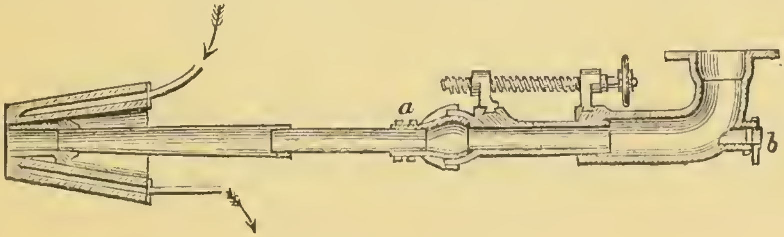

Fig. 164.

cubic feet a minute being occasionally supplied by one engine alone to a series of furnaces.

At the front of the hearth is an opening, covered by an arch, known as the *tymp*, the vertical sides of which are prolonged outwards into a rectangular cavity, called the *fore hearth*, which is fronted by a block of stone or firebrick, termed the *dam*, *b*. Over this the melted slag flows through a furrow, called the *cinder notch*, and is received into shallow trucks made of wrought-iron, in which it solidifies in rectangular blocks. When it has accumulated in sufficient quantity the molten iron is run out through a hole in the dam, which is stopped in the intervals of tapping with sand, into moulds of cast-iron or of sand.

As the furnace has to withstand the action of an exceedingly high temperature, extending in many cases over several years, great care is taken in the selection of the materials employed in its construction. The upper portion, or stack, is formed of firebricks moulded to the proper shape; outside of this ring of bricks, but with an annular space between, is a second wall, also of firebrick: the intervening space is filled with broken slag or sand, so as to allow of the contraction and expansion of the inner wall by changes of temperature. The walls of the hearth and boshes are also made of fireclay, but are of increased thickness, as they have to withstand not only the high temperature, but also the constant action of the molten slag. The whole is encased in a jacketing of wrought-iron plates, riveted together.

The capacity and relative dimensions of the furnaces in use in different districts vary very greatly, and mainly depend upon the general character of their burden. There is an obvious gain in economy in the use of tall and relatively narrow furnaces, since a great proportion of the heat carried upwards is intercepted by the mass of material above the region of active combustion. Very high furnaces, however, can only be used where the materials are sufficiently hard to resist the weight of the superincumbent mass; and in the case of soft ores and certain varieties of coal the limit of height is reached comparatively soon. In the Cleveland district, where spathic ores are mainly smelted with a very hard coke, many of the furnaces are upwards of 90 feet high. In the Ferrie furnace, which is more than 80 feet high, the fuel is coked within the shaft by the waste heat, and at the same time the burden is relieved of the superincumbent weight by an arrangement of compartments, through the openings of which the charges fall.

In setting the furnace in operation, or in "blowing in," as it is technically termed, care has to be taken to moderate the heat at first, otherwise the masonry may be cracked. A quantity of wood is placed on the hearth, and when well-lighted, coke is added, and afterwards small charges of ore and limestone, until the furnace is about one-third full. As the temperature increases and the masonry becomes dry, the charges are augmented until the furnace is in full blast, when fresh quantities of fuel, limestone, and ore, are continually added, day and night, for years, until it is necessary to "blow out" the furnace for repairs. The method of charging is by no means an unimportant matter, and various contrivances are in use to insure that the mixture maintains its proper relative proportion of fuel, ore, and lime in the various parts of the furnace. In fig. 163 one of the methods of effecting the distribution of the burden is represented: the charges striking the inverted cone, *a*, which descends into the furnace, are projected towards the sides of the stack, instead of being heaped up in the middle. The time occupied by the materials in reaching the hearth depends upon the shape and height of the furnace, and varies from about twenty-four to sixty hours. The average yield of a furnace may be stated at about 150 tons per week, and the amount of fuel needed at three times that quantity.

The following table shows the average amounts of the materials required to produce a ton of cast-iron in the principal iron-smelting districts of Great Britain :—

	Staffordshire.	Yorkshire.	Scotland.	South Wales.
	Cwts.	Cwts.	Cwts.	Cwts.
Ore, …………	40 to 60	70	36	67
Limestone, ….	15 to 18	20	10	17
Coal, …………	60	80	30	35 to 37

Formerly, the air driven into the furnace through the twyers was invariably cold, *i.e.*, of the ordinary temperature: in 1828 Mr. Neilson, a Lanarkshire iron smelter, effected a very important improvement by the substitution of hot air, whereby fuel is saved and the working power of the furnace increased. Theoretically, the hotter the blast the greater is the gain in economy; thus a saving of a quarter of a ton of coke per ton of iron made was effected by raising the temperature from 300° to 600°. The air of the blast is heated by passing through pipes surrounded by a fire, or over bricks heated by the burning of the waste gases from the furnace, which are brought down to the stoves from either the side or middle of the stack, in the manner indicated in fig. 163. The temperature of the blast may be ascertained by exposing thin rods of various metals of low fusibility in the current of the air: the rods are usually inserted in the opening *b*, fig. 164. The resistance pyrometer of Mr. Siemens might be used with greater advantage for this purpose.

The reactions which take place in the furnace are exceedingly complicated, and despite the abundant opportunities for observation from the enormous amount of iron which is produced, they are by no means thoroughly understood. The general nature of the changes experienced by the charge in its descent may be thus described:—The materials are first completely dried by the up-rush of heated gases, any carbon dioxide which may be still present in the roasted ore is expelled, and if coal be the fuel used it is gradually converted into coke. At the same time the oxide of iron begins to be reduced by the action of the carbon monoxide, so that the ore is converted into a mass of finely-divided iron disseminated through the clay and other earthy matters present in it. At a somewhat lower stage the active expulsion of carbon dioxide from the limestone commences, and lime is produced. The mass has next to be fused in order to separate the metal from the earthy matters. The reduced iron in contact with the strongly ignited fuel, hydrocarbons, and oxide of carbon, gradually combines with carbon, whereby it is rendered more fusible; at the same time it unites with silicon, phosphorus, and sulphur: the silica in the ore, existing mainly as aluminum silicate, combines with the lime, and the slag is formed. The slag and carburetted iron on reaching the boshes commence to fuse, the molten slag falls to the bottom and forms a layer through which the specifically-heavier iron sinks; as the slag accumulates and reaches the level of the dam it flows over through the cinder notch, as already described; when the amount of iron is sufficiently large for casting, the blast is stopped, and an iron bar is driven through the binding sand which stops up the tap-hole, and the fluid metal runs along the main channels, termed "sows," leading to the moulds known as "pigs," in which it solidifies.

The changes which the gaseous contents of the furnace experience have still to be traced. Commencing at the bottom where the air enters by the twyers, at a temperature of 600° or 700° C., the first action is the union of the oxygen with the carbon to form carbon dioxide, but this gas almost immediately combines with a further portion of carbon to form the monoxide, $CO_2 + C = 2CO$. At the same time, a small portion of the nitrogen of the air combines with carbon and cyanogen gas is formed, and any atmospheric moisture which is present is decomposed, free hydrogen and possibly acetylene being formed, together with carbon dioxide. All these gases in contact with the metallic iron experience more or less change: the carbon monoxide in part suffers an inverse change to that by which it was produced, being resolved into carbon dioxide and free carbon, a portion of which combines with the metal, but the greater portion of the carbon monoxide is converted into the dioxide by abstracting the oxygen from the ore in the higher portions of the stack, the carbon dioxide so formed being again partially converted into the monoxide by passing over the fuel near the throat. Similar changes are experienced by the cyanogen and the hydrocarbons, all of which doubtless assist, although probably to no very great extent, in carburetting the iron and in reducing the ore. The gases thus play very different parts in the various regions of the furnace, the difference in the reaction being mainly dependent upon the variations in temperature of the reacting materials. In addition to the gases formed by atmospheric air, we have a further quantity produced by the destructive distillation of the fuel. The general nature of the gases present in the different regions of the furnace may be seen from the following analyses of samples taken from a furnace of moderate height:—

	Distance from Mouth.		
	5 Feet.	20 Feet.	34 Feet.
Nitrogen,	55·35	60·46	58·05
Carbon dioxide,	7·77	10·82	—
Carbon monoxide,	25·97	19·48	37·43
Marsh gas,	3·75	4·40	—
Olefiant gas,	0·43	—	—
Hydrogen,	6·73	4·83	3·18
Cyanogen,	—	—	1·34
	100·00	99·99	100·00

Formerly, the whole of the gases were allowed to escape, and to burn at the throat of the furnace with a long smoky flame made luminous by the presence of hydrocarbons and suspended particles; in modern furnaces, however, they are collected and utilised as already mentioned, either for generating steam for the blowing engines and lifts, or for heating the blast and calcining the ores.

The amount of heat required to bring about these changes in the furnace is very great. Mr. Lowthian Bell has given the following table of the appropriation of heat in an eighty foot furnace during the production of 20 cwt. of pig-iron from Cleveland ore:—

	Heat Units.	
Constant requirements of furnace—		
Reduction of Fe from Fe_2O_3,	33,108	
Impregnation with carbon,	1,440	
Reduction of P, Si, and S,	4,174	
Fusion of pig-iron,	6,600	
Radiation from walls of furnace,	3,658	
Cooling twyers by water,	1,818	
Conduction to earth, etc.,	3,202	54,000
Variable sources of loss of heat—		
Fusion of slag,	16,720	
Expulsion of CO_2 from $CaCO_3$,	5,054	
Decomposition of $CaCO_3$,	5,248	
Decomposition of H_2O in blast,	2,720	
Evaporation of H_2O in coke,	313	30,055
Carried out by escaping gases,		8,860
		92,915
Brought in by hot blast,		11,919
Heat produced by combustion of coke,		80,996

The product of the furnace is known as cast or pig-iron. It is classified into grey iron and white iron according to the appearance presented by its surface when freshly fractured. This classification depends upon the state in which the carbon is present in the iron: if it exists mainly in the free state or as graphite, the iron is grey, and has a coarse-grained structure; if the carbon is chiefly in chemical union, the colour of the iron approaches more nearly to white, and the fracture is more finely-grained. White iron can only be used for forge purposes, whereas grey iron may be employed either for castings or for conversion into malleable iron. The two varieties differ considerably both in chemical and in physical properties. White cast-iron is more fusible than grey iron, but grey iron becomes more perfectly fluid when melted. White iron contracts considerably on solidification, whereas grey iron expands. White iron is specifically heavier than grey, and accordingly flows through the tapping hole first when both varieties are present in the furnace. Indeed, the smelter is generally able to determine the character of the metal from its behaviour in flowing from the furnace: white iron runs in a sluggish stream and with bright scintillations; grey iron is more perfectly fluid, and throws out very few sparks. White iron is exceedingly hard and brittle, whereas grey iron is comparatively soft and can be readily worked with a file. On dissolving grey iron in dilute nitric acid, a solution of a light-green colour is obtained, and scales of graphite remain undissolved: white iron dissolves completely and yields a brown solution; the hydrogen which is evolved has a characteristic odour due to the presence of hydrocarbons of the C_nH_{2n} series. This difference in the character of the iron is mainly dependent upon the working conditions of the furnace: the variation seems ultimately to depend upon differences in the heat of fusion and in the rate of cooling. If grey iron be remelted and suddenly cooled a considerable proportion of the carbon is found to have entered into combination, and the metal becomes white, or has a mottled appearance; not unfrequently, however, the carbon from highly-carburetted white iron is deposited as graphite on remelting. The following analyses will serve to show the extreme variability in the composition of cast-iron:—

Name of Iron.	Bowling, No. 1.	Clarence.	Northampton.
Graphite,	3·421	3·13	—
Combined carbon,	0·583	0·28	0·800
Silicon,	1·708	0·88	3·365
Manganese,	1·606	0·37	0·298
Phosphorus,	0·630	1·23	1·368
Sulphur,	0·073	0·17	0·702
Iron,	92·070	93·66	92·713

The largest amount of chemically-combined carbon in cast-iron is met with in "speigeleisen" (so named from the bright lamellar appearance it shows when fractured). This variety of iron is mainly made from spathic ores, and frequently contains a considerable quantity of manganese. It is used principally in the manufacture of steel by the Bessemer process, to be hereafter described. Its general composition may be seen from the subjoined analysis :—

Combined carbon,	4·20
Graphite,	0·42
Silicon,	0·93
Phosphorus,	0·06
Sulphur,	0·17
Manganese,	6·63
Iron,	87·59
	100·00

Conversion of Cast-iron into Wrought-iron.—The large quantities of foreign matter in cast-iron, by diminishing its toughness and tensile strength, render it unfit for many of the applications of the metal. Much of the iron made in the blast furnace requires therefore to be refined; the purified metal is called *wrought-iron.* The method of purification consists in melting the crude iron and exposing it to a stream of air. A portion of the metal is converted into oxide of iron, which parts with its oxygen to the carbon to form carbon monoxide; the silicon is simultaneously oxidised to silicon dioxide, which combines with oxide of iron to form a readily-fusible slag of ferrous silicate. The manganese, phosphorus, and sulphur, are also oxidised more or less completely, and are found in the slag or *finery cinder.* Fig. 165 represents a *refinery fire* in section, and fig. 166 shows it in plan. The oblong hearth, *a*, is formed by the junction of four iron troughs, the sides of which are kept cool by water flowing through them. The bottom of the hearth is of sand, well rammed down; it is slightly concave, and slopes towards the tapping-hole. The air, which is to effect the purification of the metal, is supplied by several twyers, usually six in number, ranged on opposite sides of the hearth. The twyers are inclined at an angle of about 30° (fig. 166), so that the blast of air may impinge directly upon the fused metal. Water runs into the cistern, *e*, and thence round the twyers, *ggg*, and into the tanks, *h h*, which also receive the water from the troughs, *b b*. Ignited coke is placed on the hearth, together with the pigs of iron to be refined; more coke is added, and the

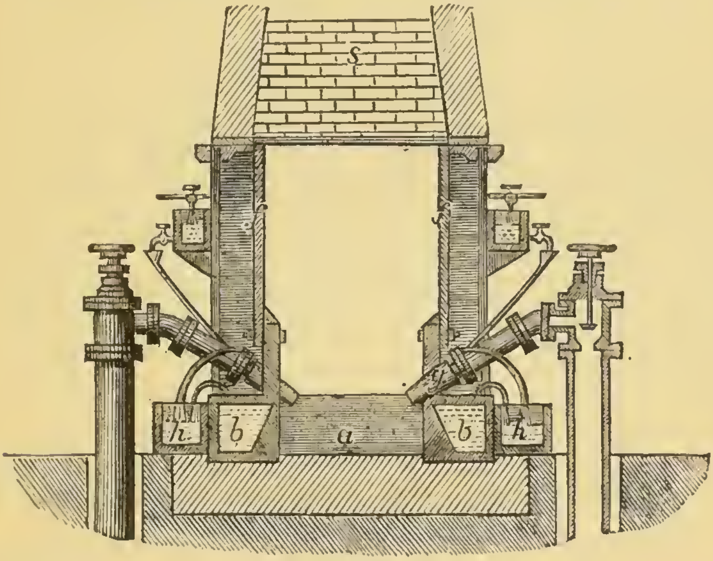

Fig. 165.

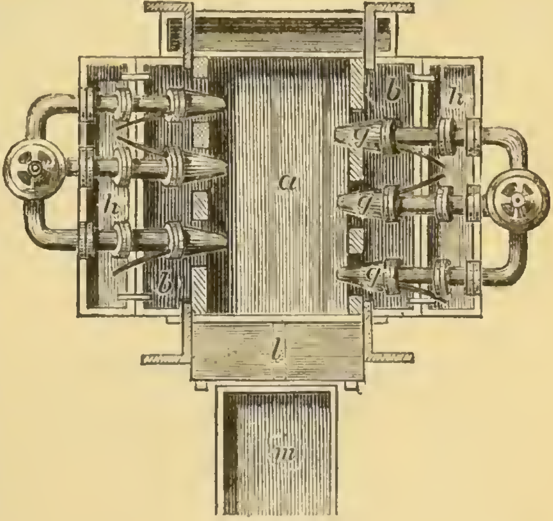

Fig. 166.

metal is melted by the aid of the blast. When a sufficient quantity of carbon has been expelled, the iron, or *fine metal,* as it is now termed, together with the slag, is run into moulds of cast-iron, cooled by water flowing round them. The layer of slag is readily detached from the solidified metal, its separation being facilitated by throwing water upon the heated mass.

From the rapid cooling of the metal, the greater portion of its residual carbon remains in combination, and the iron is rendered white. The change in chemical composition of the iron is shown in the following analyses: A is the composition of the original pig, and B that of the refined iron.

	A.	B.
Carbon,	2·40	0·30
Silicon,.	2·68	0·32
Sulphur,	0·22	0·18
Phosphorus,	0·13	0·09
Manganese,	0·86	0·24
Iron,	93·71	98·87

On the average from 22 to 25 cwt. of cast-iron are required to yield a ton of refined iron, the quantity depending upon the impurity of the pig-iron and the duration of the process. The consumption of coke is from 2 to 3 cwt., and the weight of cinder produced is about equal to that of the coke required. The general composition of the finery cinder is

Ferrous oxide,	65·52
Manganous oxide,	1·57
Alumina,	3·60
Lime,	0·45
Magnesia,	1·28
Silica,	25·77
Sulphur,	0·23
Phosphorus,	1·37
	99·79

The white iron thus obtained is still further purified by the process known as *puddling.* The main object, indeed, of the preceding operation is to convert the grey iron into white iron, since the latter variety is more readily treated in the puddling furnace than the former, on account of its own fusibility, and the peculiar pasty condition which it assumes when melted. The principle of the puddling process is, in the main, identical with that of the operation just described: a portion of the iron is first oxidised, and the oxide is incorporated with the remainder of the molten metal. Carbon monoxide is evolved, and a slag of highly basic silicate of iron, containing phosphorus and sulphur as

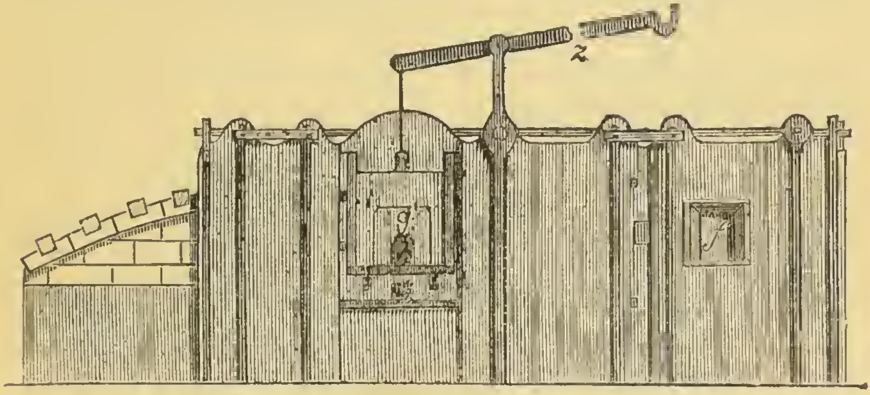

Fig. 167.

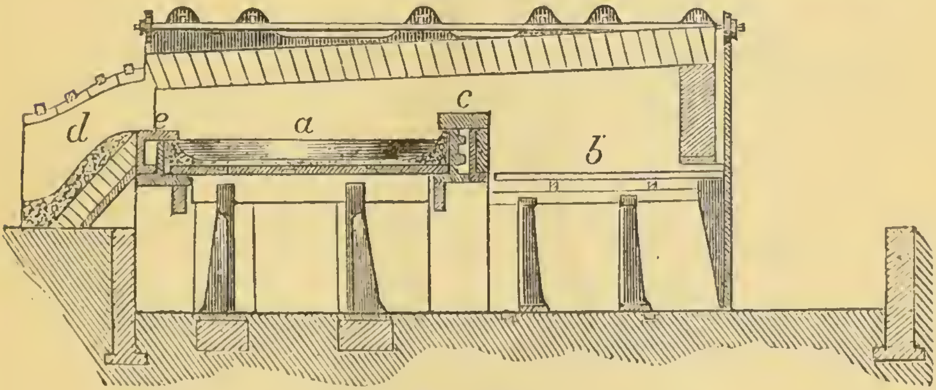

Fig. 168.

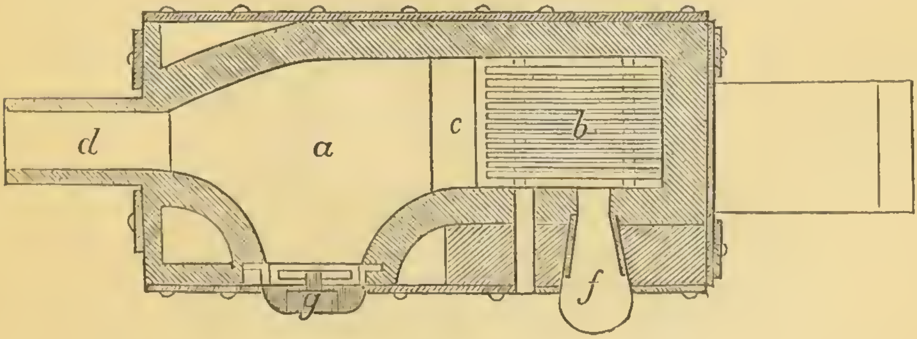

Fig. 169.

iron phosphate and sulphide, is formed. Fig. 167 represents a puddling furnace in elevation, fig. 168 in section, and fig. 169 shows it in plan. It is built of fire-brick, bound with iron tie-rods, or cased in iron plates. The fireplace is at *b*; it affords a large spreading flame which is bent down upon the hearth, *a*, from the roof; the draught through the furnace can be regulated at will by a flat plate or damper on the top of the stack. The bottom of the hearth is of cast-iron, protected from the direct action of the metal by a lining of slag, or a mixture of hæmatite and lime. The charge of iron, usually about 4 cwt., having been introduced, the heat is raised until the metal begins to soften, the masses at the sides of the hearth being moved from time to time into the middle, so that the whole may be uniformly, and as nearly

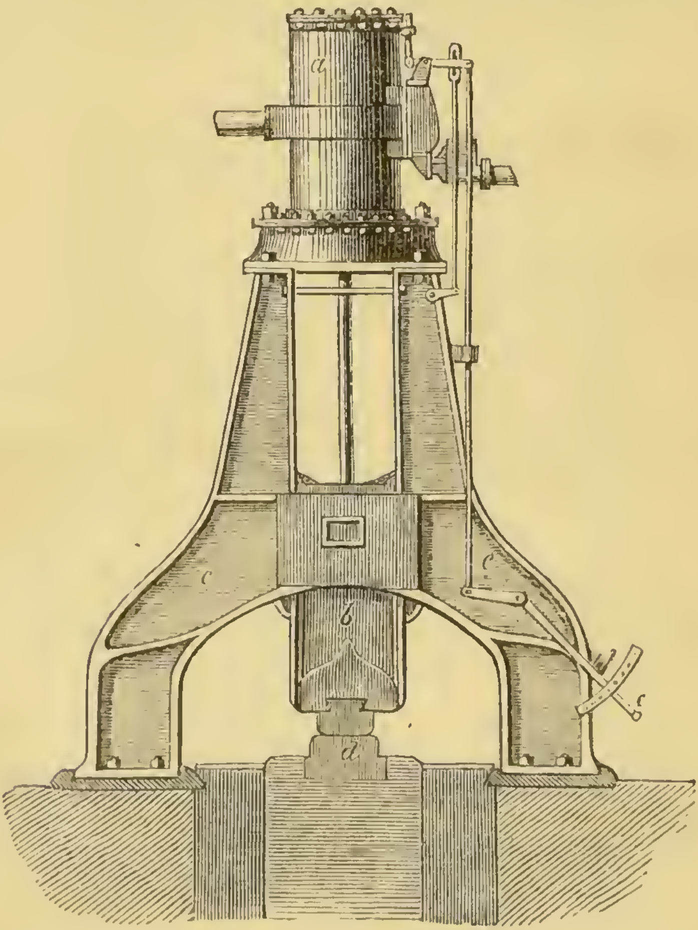

Fig. 170.

as possible simultaneously, melted. At the same time a quantity of iron scales or red hæmatite is added to the furnace. The temperature is then lowered by partially closing the damper, and the oxide is thoroughly incorporated with the metal by vigorous *rabbling* and stirring. Large quantities of carbon monoxide are evolved from the action of the iron oxide on the carbon, and the molten metal appears to boil. The ebullition gradually ceases, and small lumps of the purified metal begin to make their appearance in the bath, since the temperature of the furnace, although high enough to fuse highly-carburetted iron, is not sufficient to melt iron nearly free from carbon. The charge is now heated to the highest temperature of the furnace, and is vigorously stirred by the puddler and his assistant; the particles of softened iron are pressed together into balls weighing from 60 to 80 lbs. each, which are pushed towards the fire-bridge *c* or partition which separates the hearth from the fireplace, to preserve them from the oxidising action of the air rushing through the working door. When the charge has been worked up, the balls are dragged to the steam hammer, fig. 170, where they are subjected to a succession of rapid blows, which compress the spongy mass together, and force out the liquid slag. The metal is then

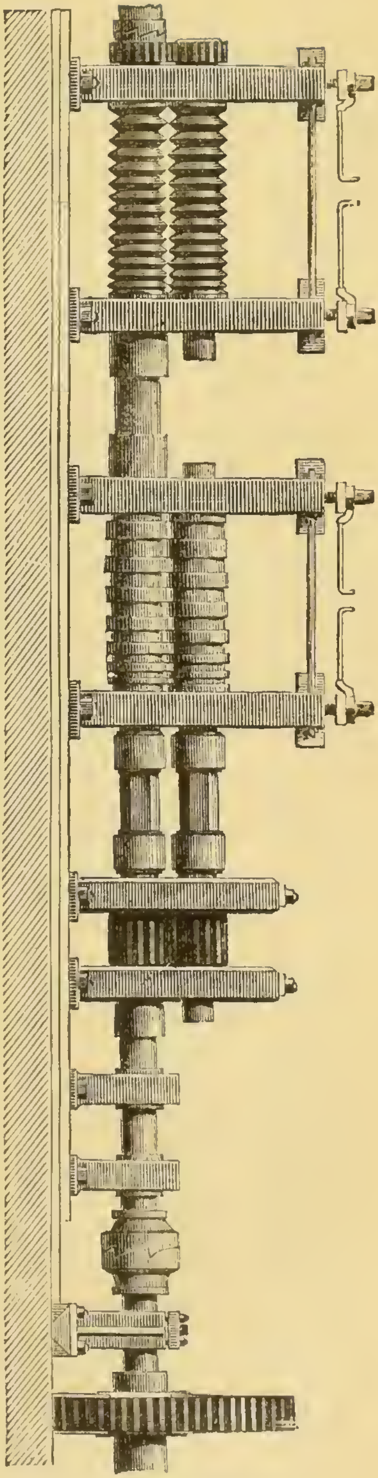
Fig. 171.

rapidly passed through the rolling mill, fig. 171, which still further reduces the size of the block or *bloom*, as it is called, and fashions it into rods, rails, or plates, as may be desired. The extent of the alteration of the pig-iron by the puddling process may be seen from the following analyses:—

	Original Pig-Iron.	Puddled Iron.
Carbon,	2·28	0·30
Silicon,	2·72	0·12
Phosphorus,	0·65	0·14
Sulphur,	0·30	0·13
Iron,	94·05	99·31

The duration of the process, and the amount of puddled metal yielded, vary with the character of the original pig; if this is very impure much longer time is needed, the waste of oxide of iron is greater, and the yield of puddled metal is proportionately diminished. The loss of weight may be stated at about 10 per cent., and the amount of coal required as about equal to that of the puddled metal produced. The general nature of the slag or *tap cinder* will be evident from the following analysis:—

Ferric oxide,	8·27
Ferrous oxide,	66·32
Manganous oxide,	1·29
Alumina,	1·63
Lime,	3·91
Magnesia,	0·34
Silica,	7·71
Sulphur,	1·78
Phosphoric acid,	8·07
	99·32

Many attempts have been made to improve the puddling process (which was introduced by Cort in 1784), more particularly with the object of lightening the labour and accelerating the operation. One of the most ingenious and successful of the proposed methods is to effect the incorporation of the oxide with the metal in a revolving cylinder lined with a mixture of lime and hæmatite. The purified iron is worked into a single ball, which is afterwards treated under the hammer as above described. The product of these operations is known as puddled bar; in order to produce what is termed finished or merchant iron, the metal has to be *re-*

heated. The bars are cut into short lengths, bound together by a wire into *piles*, and heated to the softening point on the hearth of a reverberatory or reheating furnace (fig. 172).

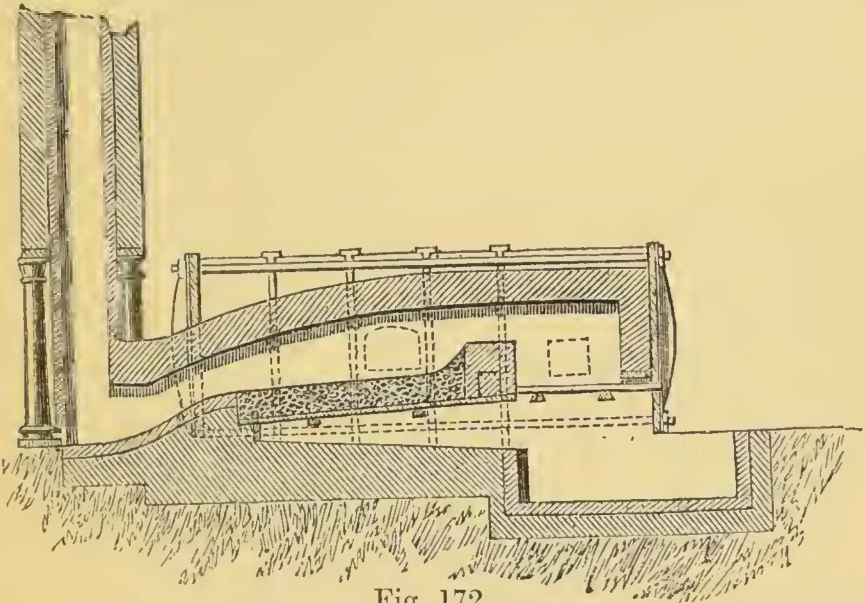

Fig. 172.

The bed of the furnace is formed of sand, and slopes gradually towards the flue, in order to allow the slag, formed by the union of the silica of the hearth with the scale of oxide of iron on the bar, to flow out at the bottom of the stack or chimney. The softened iron is then hammered and passed through the rolling mill, and is thus welded into a compact mass. The process of piling and reheating is repeated once or twice, and even oftener in the higher qualities of merchant iron. *Black plate*, or the thin iron sheet used in the manufacture of tin plate, is made by rolling out the blooms in the forge train; boiler plates, and the slabs of iron used for ships' armour, are similarly rolled and hammered.

The change in physical and chemical properties in the iron resulting from this treatment is very marked. When a rod or bar of merchant iron is notched with a chisel, and broken across by a gradual strain, it is seen to possess a peculiar fibrous structure, to which much of the great strength and ductility of the metal is probably due. Puddled bar shows no such regularity of structure; its fracture is crystalline and shining, like that of cast-iron. A stout rod of good merchant iron may be twisted and bent when cold in the most extraordinary manner without the slightest fracture; boiler plates made of such iron have been known to fold rather than break under sudden pressure. The characteristic structure of iron may be made manifest by immersing it in dilute acid for three or four days.

The influence of the substances, such as carbon, silicon, phosphorus, etc., which are invariably contained in greater or less quantity in commercial iron, has given rise to much discussion. A comparatively small quantity of sulphur in iron makes it *red-short*, that is, renders it liable to crack under the hammer at a high temperature; on the other hand, the presence of phosphorus to the extent of one part in a thousand causes the metal to crack when worked cold, or makes it *cold-short*. Cold-short iron may often be readily worked at a high temperature, and red-short iron is usually very tough when cold. Silicon, which is often present to a considerable amount in iron, greatly diminishes its tenacity. It has been found that the amount of sulphur in pig-iron is diminished as the slags formed in its production are made more basic by the addition of limestone. One of the most successful methods of removing phosphorus and silicon from pig-iron consists in running it from the blast furnace into troughs containing a thin layer of very finely-powdered fluor-spar and red hæmatite. The nature of the reaction which thus takes place is not known; it is said that fluorine is evolved from the mixture which carries off the phosphorus and silicon as phosphorus and silicon fluorides.

Production of wrought-iron directly from the ore.—The present system of manufacturing iron, which consists, as we have seen, in first making an impure metal and purifying it by refining, puddling, and reheating, owes its origin mainly to the peculiar character of our iron ores and fuel. In the early days of iron smelting, malleable iron was produced directly from the ores by a method which is still carried on in a few isolated localities where the ores are rich and readily reducible, and wood is abundant. The Catalan forge, represented in fig. 173, may be taken as a type of these early smelting hearths. The hearth is partially filled with ignited charcoal, ore is then added, and the blast is turned on.

The iron oxide is gradually reduced to the metallic state by the carbon monoxide formed, and the silica, which exists mainly as quartz in the ore, combines with another portion of oxide to form an easily-fusible slag of basic ferrous silicate which runs off through a tap-hole at the bottom; the temperature of the hearth is not high enough to fuse the metal, or even to cause it to combine with sufficient carbon to liquefy it. When the charge has been reduced, the spongy mass of iron is rolled into a ball as in puddling, and hammered into a bloom. The metal thus obtained is comparatively pure, although it usually contains more carbon than is present in ordinary wrought-iron. The amount of this constituent may, however, be diminished at will by altering the inclination of the twyer, and allowing the slag to accumulate in the hearth, conditions which are favourable to the decarbonization of the metal, and the consequent production of soft iron. Only about three-fourths of the iron in the ore is obtained as metal, the remaining fourth being expended in fluxing the silica, etc.

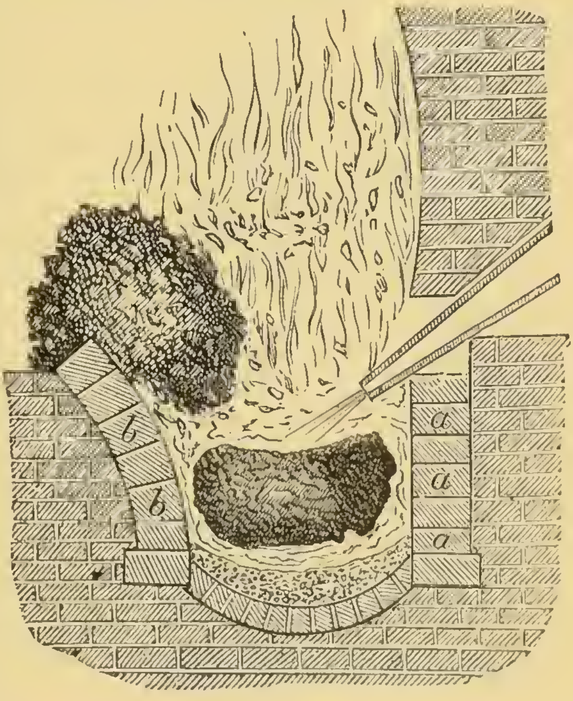

Fig. 173.

Conversion of iron into steel.—Steel is an alloy of iron with a carbide of iron: the amount of carbon may vary from 0·3 to 1·5 per cent. Below this limit it passes into wrought-iron; when containing more than the superior limit of carbon, it loses some of its distinguishing properties, and assumes those of cast-iron. In a limited sense, therefore, steel may be said to be the connecting link between cast and wrought-iron. The presence of this combined carbon in the metal renders it extremely hard and brittle after having been heated and suddenly cooled: perfectly pure iron is not altered by this treatment. If steel so hardened be again gently heated and slowly cooled, it becomes highly elastic; cast-iron may be hardened by being chilled, but it cannot be made elastic by any process of tempering. Perfectly pure iron, although highly magnetic, does not retain its magnetism; steel, however, may be made permanently magnetic, and its power of retaining magnetism appears to increase with the proportion of carbon it contains. The tensile strength of iron is also increased by an admixture of carbon up to a certain point. Ordinary bar-iron has a tensile strength of about 25 tons per square inch: the steel which is used for the manufacture of the best boiler plates contain about four parts of carbon per thousand, and has a tensile strength of from 40 to 45 tons per square inch.

Steel may be made directly from the ore, as in the Catalan forge, or from cast-iron by the refinery or puddling processes, by merely limiting the extent of the oxidation of the carbon. Unless the ores employed are exceedingly pure, the steel thus obtained is of low quality, on account of the presence of impurities. More frequently, therefore, steel is produced from refined iron by adding to it the necessary amount of carbon. Two methods of effecting this object are in common use: the refined iron is either melted with a known amount of highly-carburetted iron (speigeleisen), as in the Bessemer process; or it is simply heated to a temperature below its fusing point with carbonaceous matter, as in the cementation process.

In the cementation process bars of iron, about 3 inches broad and ¾ of an inch thick, are placed together with powdered oak or birch charcoal in rectangular chests made of flags or fire-brick, which are then exposed to a long-continued high temperature. The cementation furnace is seen in fig. 174; NN are the covered pots or troughs, round which the flame from the fireplace *c* circulates: the products of combustion make their escape through the flues EE into the dome-shaped stack F. The charge of the bar-iron is usually introduced through a man-hole, seen at G, which is walled up during the heating; a hole is left in the end of each trough through which one of the heated bars projects: this bar is withdrawn from time to time; its appearance indicates the progress of the conversion. The troughs are heated from a week to ten or eleven days; the duration depends upon the character of steel which is needed, the more highly-carburetted steels requiring the longest treatment. The assimilation of the carbon is said to commence at about 1000°, and is most active at about the melting point of copper, viz., at 1200°. From 10 to 12 tons of iron are operated upon at once, and the process occupies, on the average, about three weeks: two to three days being required for the chests to attain to the proper temperature, and nearly a week for the charge to cool down. The product of the operation is known as *blister steel*, from the peculiar appearance presented by the bars; in physical properties it differs in many respects from the original iron; its specific gravity is less, and its colour, as seen on a fractured surface, is found to have changed from a bluish-white to a reddish-white; it is less lustrous than the refined iron, and has a crystalline scaly texture. This process, in all probability, depends upon the fact that iron at

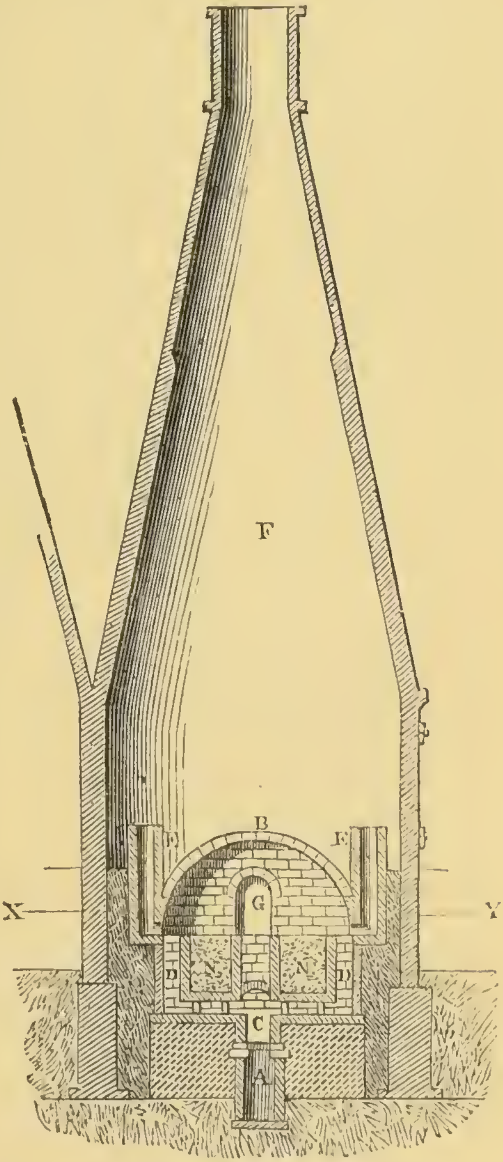

Fig. 174.

a high temperature is permeable to gases: carbon dioxide is first formed by the combination of the carbon of the cement powder with the oxygen in its pores, and this gas is converted into the monoxide by union with an additional quantity of carbon; in contact with the iron a moiety of the carbon is deposited, and the dioxide is regenerated; this, again, combines with a fresh portion of the carbon of the cement-powder, which is transferred to the metal. The oxygen of the air thus acts as a carrier of carbon to the metal.

The operation known as *case-hardening* is a rapid process of cementation, resulting in the formation of a superficial layer of steel upon the iron, and is effected by heating the iron for a few hours with carbonaceous matter containing nitrogen, as horns, bones, or scrap leather. Potassium ferrocyanide, which is obtained from such nitrogenous matter, is also frequently used. The iron is heated to redness, and the powdered salt is sprinkled over it: when suddenly cooled, the surface of the metal is found to be hard enough to resist the file.

Manufacture of cast-steel.—The steel produced by the cementation process is not very homogeneous, the internal portions of the bars being frequently much less perfectly carburetted than the external portions. In order to obtain it of uniform composition the metal is broken up, and either piled or fagotted, as in making malleable iron, when it is termed *shear-steel*, or it is melted in crucibles made of a mixture of Stourbridge or other good fire-clay and plumbago, and is poured into cast-iron moulds, forming what is known as *cast-steel.*

A small quantity of a *carbide of manganese,* produced by heating a mixture of manganese dioxide with some carbonaceous matter, such as charcoal, pitch, or resin, is occasionally added to steel in the process of melting. Although the greater portion of the manganese remains in the slag of the melting pot, the steel is rendered more tenacious than ordinary cast-steel, and may be welded to iron. A considerable quantity of cast-steel is also made directly from malleable iron by the process introduced by Mushet, that is, melting it with charcoal and manganese dioxide in clay crucibles.

Castings of steel, although apparently homogeneous, always contain internal cavities, in greater or less number, which detract greatly from the strength of the material. The formation of the flaws is obviated by subjecting the casting, whilst still hot, to intense pressure: the difference in appearance of the compressed steel and that of the ordinary casting is very striking.

Manufacture of steel by the Bessemer process.—In Bessemer's method the molten pig-iron is purified by blowing air through it; as soon as all the carbon and silicon are oxidised, a quantity of melted spiegeleisen, containing an amount of carbon sufficient to convert the iron into steel, is added. Fig. 175 represents the egg-shaped vessel or *converter* in which the process is carried on. It is made of wrought-iron plates riveted together, and is lined with some refractory material, highly siliceous sandstone from the coal measures, called *ganister*, being usually employed. The ganister, previously ground to powder, is moistened with water to make it cohere, and rammed down between the iron shell and a wooden cone, placed temporarily within.

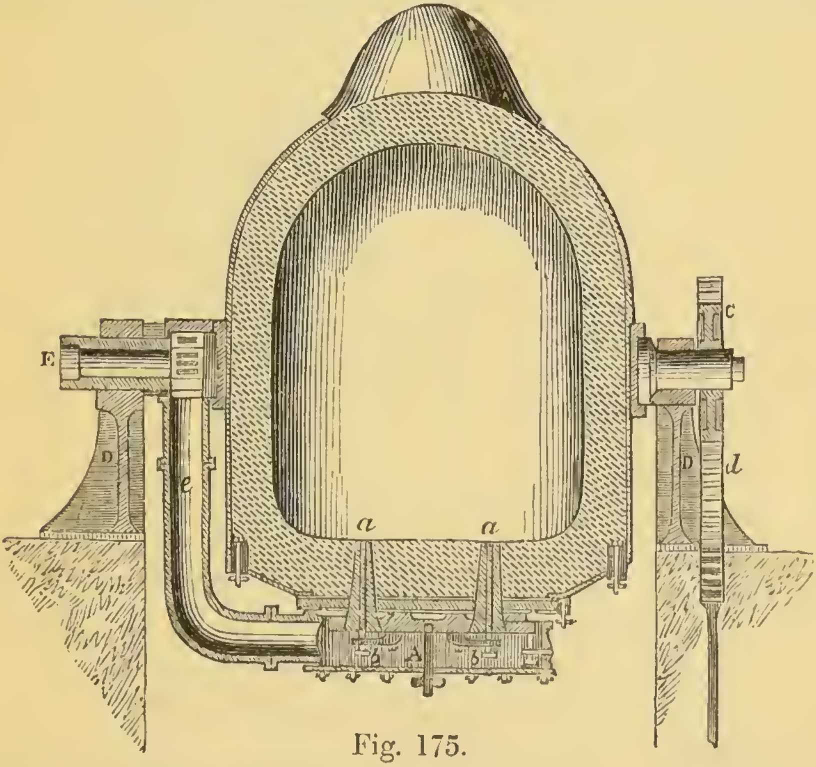

Fig. 175.

The converter is supported on trunnions, and can be turned vertically through an angle of about 180° by a hydraulic engine, to the piston-rod of which is attached a rack which works on the pin of the trunnion, as seen in fig. 175. The air-blast passes up the hollow trunnion E and along the pipe *e*, and enters the converter through a number of holes in the fire-brick twyers *a a*. The converter is first partially filled with ignited coke to heat the lining to redness; it is then tilted over to throw out any residual fuel, and the charge of 5 or 6 tons of molten pig-iron is run into it. The blast is turned on, and the converter raised to a vertical position. A sheet of flame is seen to issue from the mouth of the converter: its colour is at first yellow or orange, but it gradually changes to blue or violet, as the amount of carbon monoxide increases. The changes in the appearance of the flame are indicative of the nature of the reactions within the converter. The graphite in the molten pig is first converted into combined carbon; at the same time the silicon is oxidised, and combines with iron and manganese oxides, forming a cinder similar in composition to that of the puddling furnaces. In about five minutes after the commencement of the "blow," the flame is seen to increase in brilliancy, and showers of sparks issue from the converter: these consist of particles of iron and slag projected from the molten mass. The contents of the converter are in a state of violent ebullition, due to the energy of the reaction of the iron oxide upon the carbon, resulting in the rapid disengagement of carbon monoxide. The reaction now proceeds more quietly until, after about eighteen or twenty minutes blowing, the flame is seen to drop from the cessation of the evolution of the carbon monoxide, a point which may be ascertained with great ease and certainty by the disappearance of certain lines in the spectrum of the flame, due to oxide of manganese. The converter is now swung down to the horizontal position, the proper charge of speigeleisen introduced, and the contents of the converter emptied into the ladle (fig. 176). The ladle is next brought over the cast-iron ingot moulds, placed on the bottom of the casting pit, and the molten metal is allowed to flow out by raising a fire-clay plug at the bottom, the specifically lighter slag floating at the top.

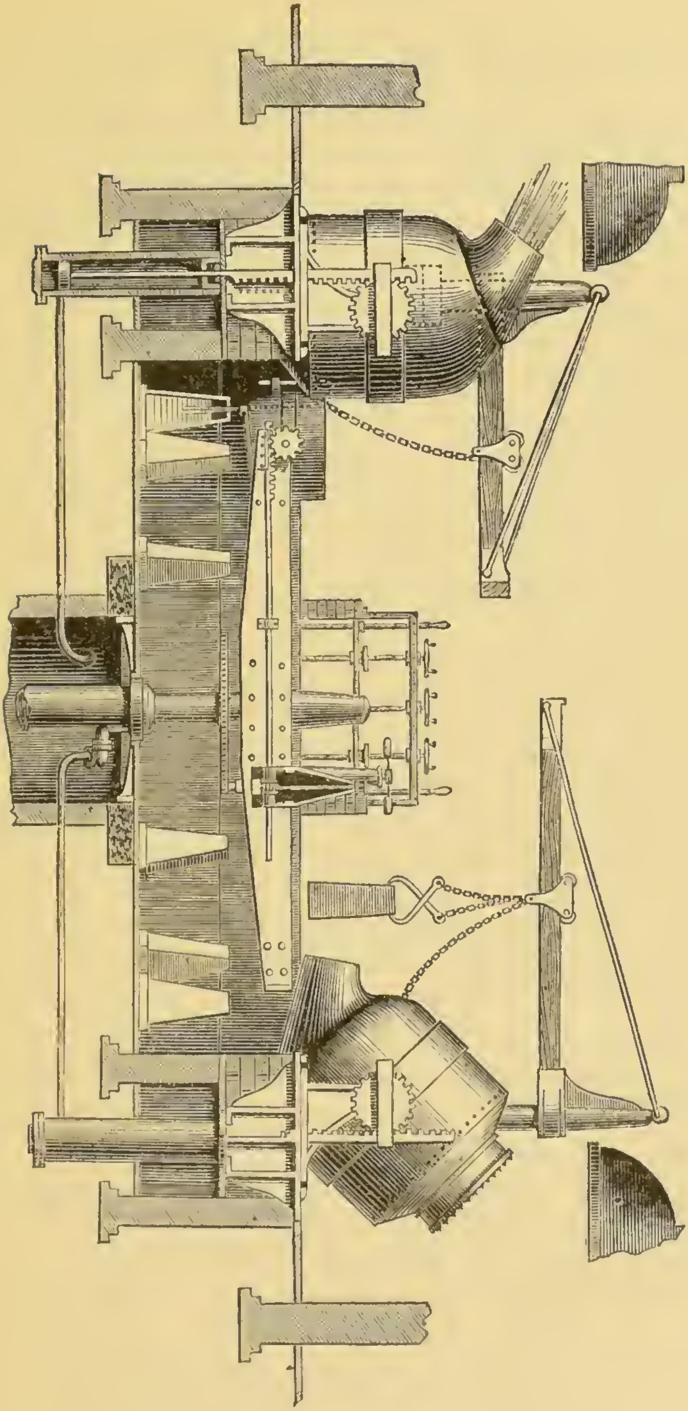

Fig. 176.

In manufacturing steel by the Bessemer method, it is essential that the pig-iron to be operated upon shall be as free as possible from sulphur and phosphorus, since the greater portion of these impurities remain in the iron at the conclusion of the blow, and detract from the quality of the metal. A minute portion of silicon seems to prevent the rapid disengagement of gas from the steel after it has been poured into the ingot mould, and thus tends to produce sound ingots; in practice it is found that the requisite quantity of silicon is contained in the speigeleisen added.

Enormous quantities of Bessemer steel are now made for conversion into rails and railway tires. The cast-iron is run directly from the blast furnace into the converter; and the steel ingots, obtained as described, are placed in a reheating furnace, in contact with a smoky flame to prevent burning, passed through the rolling mill, and fashioned into the required shape by the finishing mill.

The proportion of carbon in the steel has such an important influence upon its properties that it is constantly necessary to determine its amount by chemical analysis. The most simple and expeditious process is that due to Eggertz. It is founded on the fact, already mentioned, that iron containing combined carbon dissolves in nitric acid with a brown colour, the depth of which is proportionate to the quantity of carbon present. The colour produced is then compared with that of a standard tint, equivalent to a known quantity of carbon. Two thin test-tubes, made of the same glass, are graduated into tenths of a cubic centimetre. One decigram of steel or wrought-iron, the amount of carbon in which is accurately known, is placed in a test-tube, and covered with about 2c.c. of moderately dilute nitric acid; a decigram of the steel or iron, the amount of carbon in which has to be determined, is similarly treated in a second test-tube. Both tubes are gently heated until all action is at an end, when the brown solutions are decanted into the graduated tubes. Let us assume that the standard iron contains 0·5 per cent. of carbon; its solution is therefore diluted until it measures 5c.c.: 1c.c. is equivalent to 0·0001 gram carbon. Water is added, drop by drop, to the solution of the iron to be compared until the depth of colour is equal to that of the standard; since each cubic centimetre is equal to 0·1 per cent. of carbon, a simple inspection of the volume of the solution in cubic centimetres indicates the percentage amount of carbon contained in the sample under examination: thus, supposing the volume of the solution was 3·5 c.c, the iron would be said to contain 0 35 per cent. of combined carbon.

Pure iron is a comparatively soft, tenacious, highly-malleable metal of a silvery lustre, and conchoidal or crystalline fracture. According to Caron, its specific gravity, after fusion in hydrogen, is 7·880; when forged, 7·868; when drawn into wire, 7·847. Iron, obtained by electrolysis, has a specific gravity of 8·139. The pure metal is not hardened by being heated and rapidly cooled; and it dissolves in acids with the production of hydrogen free from odour. It appears to rust more readily than ordinary malleable iron. The rusting of iron is primarily due to the action of carbonic acid, and not simply to moisture and oxygen: it appears that the metal readily combines with moist carbonic acid forming the normal carbonate, which is quickly oxidised to ferric oxide in presence of moist air, the liberated carbonic acid attacks a fresh portion of the metal, and more oxide is formed, so that eventually the whole becomes converted, by the alternate formation of carbonate and oxide, into a loosely coherent mass. The behaviour of iron with nitric acid is very remarkable. The nature of the reaction varies with the dilution of the acid, and with its temperature. With very dilute acid hydrogen is evolved, and a ferrous salt is produced; if the acid is stronger or the solution becomes heated, nitrogen dioxide is formed, together with a ferric salt. Nitric acid, of a certain degree of concentration, and at a particular temperature, has no action upon iron; that is, the metal becomes *passive*. The temperature at which this phenomenon occurs depends upon the strength of the acid: with nitric acid of specific gravity 1·38, it is at 31°; with colourless acid of specific gravity of 1·42, it is at 55°. The presence of lower oxides of nitrogen in the acid also influences the temperature at which the iron becomes passive: thus with red fuming acid of specific gravity 1·42, the metal is unacted upon up to 82° (Ordway). The effect of cold upon malleable iron has been variously stated: the experience of railways in countries where the winters are severe seems to indicate that a very low temperature diminishes the elasticity and tenacity of the metal, and thus occasions the snapping of wheel tires and axles. On the other hand, the experiments of Fairbairn, Joule, and Caron, made with the special view of testing this point, fail to show that intense cold has any such action on iron.

320. Iron unites with oxygen to form ferrous oxide, FeO, and ferric oxide, Fe_2O_3: a number of compounds intermediate between these are known, chief among which is the magnetic oxide or triferric tetroxide, Fe_3O_4. A trioxide, FeO_3, exists in combination, giving rise to a series of salts, termed ferrates: the oxide itself, however, is not known in a separate state.

Ferrous Oxide, FeO or Fe_2O_2, is a black powder, obtained by heating the metal in carbon dioxide:

$$Fe + CO_2 = CO + FeO;$$

or by partial reduction of the ferric oxide, or by heating the oxalate out of contact with oxygen. It is very unstable, and takes fire on exposure to air, especially when heated, forming ferric oxide. **Ferrous hydrate** is obtained as a white precipitate by mixing solutions of a ferrous salt and caustic potash both perfectly free from air. It rapidly absorbs oxygen, even when dry, becoming hot, and changing to ferric oxide; it appears to be very slightly soluble in water; its solution has an alkaline reaction, and absorbs carbonic acid. Both the oxide and the hydrate are attacked by the greater number of acids, forming ferrous salts, which are usually white when anhydrous, and green or greenish-blue when hydrated.

Ferric Oxide, Fe_2O_3, is exceedingly abundant in nature, and forms one of the principal sources of the metal. Some of its varieties, *e.g.*, red hæmatite and specular ore have already been mentioned. It is obtained artificially by a variety of processes, and is frequently procured as a bye-product in manufacturing operations, as in making sulphuric acid from pyrites, etc. The *caput mortuum vitrioli* of the alchemists, obtained by heating ferrous or ferric sulphate in the preparation of fuming sulphuric acid, is ferric oxide (see

Vol. I., p. 327). The *ferrum oxydatum rubrum* of pharmacy is also ferric oxide, prepared by heating ferric hydrate or ferrous carbonate in contact with air. The preparations thus obtained are exceedingly hard, and are much used as polishing powders. Ferric oxide is also used to colour glass and porcelain; it gives an orange or a purple-red colour, according to the temperature and mode of treatment.

In the amorphous state, ferric oxide is a red or brownish-red, or even black powder; the particular colour depends upon the manner of its preparation. Its specific gravity is also variable: the extremes recorded are 4·679 and 5·283. According to Elsner it can be volatilised in the heat of a porcelain furnace; at a very high temperature it is partially converted into a ferroso-ferric oxide. It is readily reduced on heating with hydrogen, carbon monoxide, or ammonia. Sulphuretted hydrogen converts it into a sulphide: pseudomorphs of iron pyrites, derived from hæmatite or specular ore, are occasionally found native. **Ferric hydrate** also occurs naturally in large quantities, as *limonite*, *göthite*, etc., and may be prepared by mixing solutions of ammonia or caustic potash with a ferric salt. It is a yellowish or brownish-red powder, its colour varying with the manner of its preparation and degree of its hydration. Both the oxide and the hydrate are soluble in acids, especially in hydrochloric acid: by prolonged heating the solubility of the oxide is greatly diminished. If the brownish-yellow ferric hydrate, prepared by adding ammonia to ferric chloride, be boiled with water for several hours its colour changes to brick-red, and it becomes difficultly soluble in strong nitric or hydrochloric acid. Dilute acids dissolve it, forming a dark-red liquid which appears to be turbid when seen by reflected light; on the addition of a strong acid, or a solution of common salt, it forms a red precipitate which dissolves on immediate dilution with water. If the precipitate be left for some days in contact with the saline liquid it becomes insoluble. The solution in acetic acid, after being heated for some time, is not darkened in colour on the addition of a sulphocyanate, nor does it form Prussian blue with potassium ferrocyanide solution (Péan de Saint-Gilles). A solution of this modified oxide in hydrochloric acid, when submitted to dialysis, is dissociated, ferric oxide soluble in water remains on the dialyser, and hydrochloric acid passes through into the outer liquid.

Ferric hydrate is reduced by organic matter in process of decomposition, but in contact with air it is quickly reoxidised; it thus acts as a carrier of oxygen from the air to the organic substance, and greatly promotes its decomposition: the rapid decomposition of humus and woody fibre in many ferruginous soils is thus brought about. Ferric hydrate behaves like alumina in contact with many colouring matters, and is accordingly used as a mordant; its affinity for organic matter is seen in the formation of iron-mould on linen, cotton, etc.

Ferric salts are usually white when anhydrous, and yellow or reddish, or brownish-yellow in the hydrated state. In solution their colours are extremely variable: the nitrate and fluoride are colourless; the chloride is brown-red; and the acetate, sulphocyanate, and meconate are deep-red. The addition of hydrochloric acid to ferric chloride solution changes its colour to intense yellow, especially on heating: this colouration is destroyed on the addition of sodium phosphate.

Ferroso-ferric Oxides.—A number of oxides of the general formula Fe_nO_{n+1}, intermediate in composition between ferrous and ferric oxides, are classed together under this name. When a piece of iron is heated to redness in air a "scale" is formed upon its surface, the composition of which varies with the thickness of the mass and the duration of the heating. The outer portions of the "scale" are always more oxidised than the inner portions: the innermost layers have a constant composition, represented by the formula Fe_8O_9, *i.e.*, $6FeO.Fe_2O_3$: the amount of ferric oxide in the outer layers varies between 30 and 50 per cent. Products of this character are constantly met with in the hearths and beds of furnaces employed in the manufacture of iron: a mass of steel-grey crystals occurring in a Carinthian blast furnace was found by H. Völker to have the composition $Fe_{11}O_{12} = 9FeO.Fe_2O_3$.

Triferric Tetroxide, or Magnetic Oxide of Iron, $Fe_3O_4 = FeO.Fe_2O_3$, is one of the most valuable ores of iron (p. 337). It is formed artificially when iron is heated to redness in steam, or when it is burned in oxygen gas: as thus obtained it is a black, amorphous, strongly-magnetic mass. It may be obtained in octahedrons, together with ferrous chloride, by heating ferrous oxide in a slow stream of hydrochloric acid gas; by heating ferrous sulphite with calcium chloride in a covered crucible; or by fusing ferric phosphate with sodium sulphate.

The *Æthiops martialis* of pharmacy is a variable mixture of ferrous and ferric oxides, made by igniting ferric oxide with iron filings or with oil.

A number of **ferroso-ferric hydrates** are also known. The dingy green colour which moist ferrous hydrate assumes in contact with air, is due to the formation of one of these bodies. It is very unstable, and quickly passes into the red ferric hydrate. A **black hydrate**, of the composition $Fe_2O_3.FeO + xH_2O$, is formed by dissolving the magnetic oxide in hydrochloric acid and adding ammonia, or by mixing ferrous and ferric salts, adding ammonia, and boiling. The moist ferroso-ferric oxide has a remarkable power of absorbing certain salts and organic matters from solution: when the oxide is ignited its absorbent power is greatly diminished. This property may possibly be taken advantage of in the purification of water. The oxide is magnetic even when moist. It is doubtful if the ferroso-ferric oxides or hydrates, when dissolved in acids, yield definite salts: the probability is that the solutions are merely mixtures of ferrous and ferric salts.

321. Ferrates.—These salts are assumed to contain ferric oxide, FeO_3, but neither this compound nor the corresponding acid, H_2FeO_4, have yet been isolated.

The formation of a purple-coloured solution when iron is heated with nitre and the mass treated with water, appears to have been observed by Stahl, but the true nature of the compound thus formed was first demonstrated by Fremy in 1840: he showed it to consist of **potassium ferrate**, K_2FeO_4. This body is formed by throwing a mixture of 1 part of iron filings and 2 parts of nitre into a crucible heated to dull redness: on treating the residue with water the ferrate dissolves. A readier method consists in suspending ferric oxide in a very strong solution of caustic potash and passing chlorine into the liquid; the oxide is gradually converted into potassium ferrate, which, being almost insoluble in the strong alkaline liquid, separates out as a black powder, which may be dried on a porous tile. It is soluble in water, forming a deep cherry-red solution, which is almost opaque, except when seen in thin layers. The solution is stable when concentrated, but on dilution it readily decomposes with evolution of oxygen and precipitation of ferric oxide. Reducing agents and organic matter also decompose it; sulphuretted hydrogen and ammonium sulphide turn the strong solution green; on heating it becomes brown, but the green colour is restored as the liquid cools.

Barium Ferrate, $BaFeO_4$, is a deep-red powder, formed by adding barium chloride to a solution of potassium ferrate. It is moderately stable, and may be heated to 100° without alteration, even when moist, and is soluble in acetic acid without decomposition.

322. **Ferrous Chloride**, $FeCl_2$ or Fe_2Cl_4, is obtained anhydrous by cautiously heating sublimed ferric chloride in dry hydrogen gas; by passing chlorine over excess of iron filings; or by heating finely-divided iron with sal-ammoniac. It forms white crystalline deliquescent scales of specific gravity 2·528 (Filhol); it melts at a red heat, and may be sublimed. It is readily soluble in water and alcohol. It is decomposed on heating with aqueous vapour, forming triferric tetroxide, hydrochloric acid, and free hydrogen:

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2.$$

It absorbs ammonia gas, forming **ferrammonium chloride**, which, on exposure to moist air, yields **ferric oxychloride** and **ferric-ammonium chloride**, $4NH_4Cl.Fe_2Cl_6.2H_2O$. Ferrammonium chloride, heated nearly to redness, yields **iron nitride**, N_2F_4, in thin laminæ, or as a grey powder: this compound is slowly decomposed by boiling water, and forms ammonia and ferroso-ferric oxide when heated in aqueous vapour. Ammonia is likewise formed when the nitride is heated in hydrogen gas. According to Stahlschmidt this substance may also be obtained by the action of ammonia gas on metallic iron, or on ferric oxide; he is of opinion that it is occasionally present in steel.

Hydrated ferrous chloride, $FeCl_2.4H_2O$, is readily obtained in bluish-green monoclinic crystals by concentrating a solution of iron in hydrochloric acid. The salt unites with the alkaline chlorides to form compounds which may be regarded as derived from the hydrate by partial replacement of the water of crystallization. The salts actually prepared have the formulæ $FeCl_2.2KCl.2H_2O$. and $FeCl_2.2NH_4Cl.2H_2O$. A remarkable compound of the composition $FeCl_2.C_2H_4.2H_2O$. is known: it is obtained by heating an ethereal solution of ferric chloride to 150°; it is readily soluble in water, and rapidly oxidises on exposure to air.

Ferric Chloride, Fe_2Cl_6, has been observed to occur in the craters of active volcanoes, and may be obtained artificially by the direct union of chlorine and iron, or by dissolving iron in hydrochloric acid and treating the solution with chlorine gas, evaporating to dryness, and heating the residue, when the chloride sublimes and condenses in the form of black iridescent deliquescent laminæ. Ferric chloride is readily soluble in water with considerable rise of temperature: it forms a dark-brown liquid, which on evaporation yields crystals containing a variable amount of water. The solution is decomposed on heating, especially if dilute, into the modified (colloidal) ferric oxide, which remains in solution, and free hydrochloric acid. If the solution be moderately concentrated, and the temperature be maintained below 120°, the ferric oxide and hydrochloric acid recombine on cooling, forming ferric chloride; at high temperatures ferric oxychloride, and eventually insoluble ferric oxide, are formed. In the case of very dilute solutions (below 2 per cent.) the dissociation takes place below 100°, and the colloidal oxide and free acid remain separate on cooling. This dissociation takes place even in strong sunlight and at ordinary temperatures, in solutions of less than one-sixteenth per cent. strength.

Ferric chloride is reduced to ferrous chloride by sulphur dioxide, stannous chloride, metallic zinc, silver, and platinum, and many organic substances. It is soluble in alcohol and ether. Its solution readily coagulates albumen, and it is used in medicine on account of its strong styptic action.

A solution of ferric chloride dissolves considerable quantities of ferric hydrate, with formation of a deep-red liquid, due to the presence of basic chlorides of variable composition.

Ferric chloride combines with the alkaline chlorides to form double salts, and it absorbs ammonia gas with rise of temperature, producing $2NH_3.Fe_2Cl_6$. It also unites with cyanogen chloride and phosphorus pentachloride.

Bromine unites with iron to form **ferrous** and **ferric bromides**, which are similar in properties and constitution to the corresponding chlorides.

323. Ferrous Iodide, FeI_2, which is used to some extent in medicine, is readily prepared by triturating iron with iodine and water. Its solution yields green crystals of the composition $FeI_2.5H_2O$, which become brown on exposure to air, from the separation of iodine and ferric oxide. The solution dissolves iodine, forming a brown liquid; ferric iodide has, however, not yet been satisfactorily isolated.

324. Ferrous Fluoride, $FeF_2.xH_2O$, is formed by dissolving iron in hydrofluoric acid; it crystallises in thin colourless plates, which may be dried without decomposition. It combines with alkaline fluorides to form double salts of the general formula $FeF_2.2MF$.

Ferric Fluoride, Fe_2F_6, is obtained by dissolving ferric hydrate in aqueous hydrofluoric acid. It forms stable flesh-coloured crystals, which melt readily and may be volatilised, and it unites with the alkaline fluorides to form double salts. No compound analogous to cryolite has, however, yet been prepared.

325. Octoferric Sulphide, Fe_8S, is a dark-grey magnetic powder, formed by passing hydrogen gas over strongly-heated basic ferric sulphate. Dehydrated ferrous sulphate, similarly treated, yields a **hemisulphide**, Fe_2S, which is also magnetic: this body is obtained as a bye-product in lead and copper smelting.

Ferrous Sulphide, FeS, is not known to occur native in the free state, except in meteoric iron, constituting the so-called *triolite*. It is found, however, in a state of combination with nickel and copper sulphides in certain Norwegian minerals. It may readily be obtained artificially by the direct union of sulphur and iron: sulphur vapour passed over heated iron combines with the metal, and a roll of sulphur pressed against a rod of iron heated to redness forms fused ferrous sulphide. The two elements combine, even at ordinary temperatures, if finely divided and moistened. As usually obtained, it forms a black porous mass, but it is occasionally produced in minute crystals resembling quartz. It may be heated to whiteness in closed vessels without alteration: heated in contact with air it is converted into a mixture of ferrous sulphate and ferric oxide. On the addition of hydrochloric or sulphuric acid it evolves sulphuretted hydrogen. The mud which forms at the bottom of cesspools and drains mainly owes its black colour to the presence of ferrous sulphide, formed by the reduction of sulphates by decomposing organic matter in presence of iron oxides, either in the water or in the soil.

Ferric Sulphide, Fe_2S_3, is formed by heating iron with excess of sulphur: it is a yellowish-grey non-magnetic powder. It exists in nature in union with copper sulphide, forming copper pyrites, $Cu_2S.Fe_2S_3$.

Ferroso-ferric Sulphide, or **Magnetic Pyrites**, is found native in tabular crystals belonging to the hexagonal system, of a brownish-yellow colour. It is slightly magnetic, tarnishes in the air, and is dissolved by acids with evolution of sulphuretted hydrogen and separation of sulphur. Heated with strong alkalies, a portion of the sulphur is abstracted and ferrous sulphide remains. The ferroso-ferric sulphides may be classed under the generic formula $Fe_nS_n + Fe_nS_{n+1}$, the most commonly-occurring proportions being $Fe_3S_4 = Fe_2S_3.FeS$, $Fe_7S_8 = 5FeS.Fe_2S_3$, and $Fe_8S_9 = 6FeS.Fe_2S_3$, the latter corresponding to the "scale oxide."

Iron Disulphide, FeS_2.—This compound occurs naturally in two distinct forms, viz., as *yellow iron pyrites* or *mundic*, which crystallises in forms derived from the regular system; and as *white iron pyrites*, or *marcasite*, which is found in triclinic crystals. The conditions which determine the formation of the particular variety are unknown.

Mundic is heavier and much more permanent in the air than marcasite. Its streak is brownish-black, whereas that of marcasite is a dark greenish-grey. Both forms when finely divided and in contact with water undergo rapid oxidation, with considerable rise of temperature; seams of coal, and lignite rich in iron pyrites, have occasionally been ignited from this cause. The water derived from coal mines frequently contains considerable quantities of ferrous sulphate, derived from the oxidation of the disulphide: the ferrous sulphate met with in certain mineral waters is probably formed in the same manner.

Iron disulphide may be formed artificially as a dark-yellow powder by gently heating any of the oxides of iron in a stream of sulphuretted hydrogen until sulphur is no longer absorbed, or in brass-yellow cubes by heating a mixture of sulphur, sal-ammoniac, and ferric oxide.

Selenium also unites with iron in varying proportions, but the only combination of which the composition is known is the **ferric selenide** Fe_2Se_3, a greyish-yellow brittle substance of sp. gr. 6·38.

326. Ferrous Sulphite, $FeSO_3$, is obtained in green crystals containing 3 molecules of water by evaporating the solution of iron or ferrous carbonate in aqueous sulphurous acid. Normal ferric sulphite is not known; ferric hydrate dissolved in aqueous sulphurous acid yields a blood-red liquid which quickly changes to a solution of ferrous sulphate. On the addition of alcohol to the red solution, a basic salt of the composition $\left.\begin{matrix}(SO)_3\\Fe_4\end{matrix}\right\}O_9$ is precipitated.

327. Ferrous Sulphate, or **Green Vitriol,** $FeSO_4$, is occasionally found native as a product of the oxidation of iron pyrites, and may be readily obtained artificially by dissolving iron in dilute sulphuric acid. Much of the green vitriol of commerce is obtained as a bye-product in the manufacture of alum from aluminous schist (see p. 241). The degree of hydration of the salt depends upon the strength of the solution, the temperature of the liquid, and the amount of free acid present. The salt usually contains 7 molecules of water, and forms monoclinic crystals of a bluish-green colour, which are tolerably permanent in air if not too dry or too moist; in the former case the salt loses water; in the latter it becomes coated with a brownish crust of ferric sulphate. The salt loses 6 molecules of water by prolonged drying at 100°, but retains the seventh up to 300°. Anhydrous ferrous sulphate may be formed by boiling the ordinary salt with strong oil of vitriol. A solution of ferrous sulphate mixed with oil of vitriol, and placed *in vacuo*, gradually deposits the salt with diminishing quantities of water of crystallization; a pentahydrate in triclinic crystals; a tetrahydrate in monoclinic crystals; a trihydrate and a dihydrate (the latter isomorphous with the dihydrated calcium sulphate) may be thus obtained. The prolonged action of the sulphuric acid gives rise to the formation of white crystals of ferrous anhydrosulphate, $FeS_2O_7 = FeSO_4.SO_3$. The heptahydrated salt requires about 1·5 parts of cold water, and one-third of its weight of boiling water, for solution. The liquid has a light bluish-green colour, and gradually oxidises by exposure to air. It may be preserved unaltered by suspending scraps of iron wire in the liquid. The solution absorbs the dioxide and trioxide of nitrogen, forming a dark-brown solution which rapidly absorbs oxygen; the production of this colour is used as a test for nitric acid (Vol. I., p. 203). Ferrous sulphate forms double salts with the alkaline sulphates of the general formula $FeSO_4.M_2SO_4.6H_2O$; a molecule of water in the heptahydrated salt being replaced by a molecule of the alkaline sulphate. These salts are occasionally used to determine the strength of the permanganate and bichromate solutions employed in volumetric analysis (see p. 343).

Ferric Sulphate, $Fe_2(SO_4)_3$, occurs native as the mineral *Coquimbite* found in Chili; it has been found in small violet-coloured crystals as a deposition in the platinum retorts employed in concentrating oil of vitriol. It is almost insoluble in water and hydrochloric acid. The hydrated salt may be obtained by dissolving ferric hydrate in sulphuric acid, or by adding nitric acid in small quantity to a solution of ferrous sulphate. On evaporation it yields a brownish-yellow deliquescent mass which is readily soluble in water. A number of basic salts are formed by adding ferric hydrate to a solution of the ferric sulphate, or by allowing ferrous sulphate to oxidise by exposure to air. Ferric sulphate forms double salts by union with various sulphates; some of these are used in the arts. **Iron-ammonium alum,** or **ammonio-ferric sulphate,** $\left.\begin{matrix}Fe_2\\(NH_4)_2\end{matrix}\right\}4SO_4.24H_2O$, is used in dyeing. A corresponding potassium compound exists, but it is less stable. Both these compounds give rise to a variety of basic salts: a salt of the composition $4(Fe_2O_3.SO_4).(K_2SO_4)9H_2O$ has been found native in certain Bohemian lignites; and a similar sodium compound occurs in alum shales.

328. **Ferrous Nitrate**, $Fe2NO_3$, may be obtained by mixing solutions in equivalent quantities of ferrous sulphate and barium nitrate, or, with simultaneous formation of ammonium nitrate, by dissolving iron in cold dilute nitric acid (sp. gr. 1·034):

$$Fe_4 + 10HNO_3 = 4Fe2NO_3 + NH_4NO_3 + 3H_2O.$$

This solution is used in dyeing; when concentrated it yields greenish deliquescent crystals.

Ferric Nitrate, FeN_3O_9, is formed by first dissolving iron in nitric acid of sp. gr. 1·3, and then adding to the solution a quantity of still stronger acid (sp. gr. 1·43), when the salt separates out in colourless prismatic crystals containing either 6 or 9 molecules of water. The crystals melt at a low temperature, and lose nitric acid when heated above 100°. Ferric nitrate solution dissolves considerable quantities of ferric hydrate, forming basic nitrates.

329. **Iron Phosphides.**—Three of these compounds are known, viz., Fe_4P_2, Fe_2P_2, and Fe_3P_4. The compound Fe_4P_2, corresponding to the only known nitride, is a light-grey crystalline non-magnetic powder of sp. gr. 5·74; it may be heated in hydrogen or carbon monoxide without alteration. It is obtained by strongly igniting a mixture of ferric phosphate and lampblack, and treating the mass with dilute hydrochloric acid. The phosphorus in pig-iron probably exists in this form. The phosphide, Fe_2P_2, is formed by heating ferrous sulphide or ferric chloride in phosphine:

$$2FeS + 2PH_3 = Fe_2P_2 + 2H_2S + H_2.$$
$$Fe_2Cl_6 + 2PH_3 = Fe_2P_2 + 6HCl.$$

It is a dark-blue powder which burns when heated in the air, and is reduced on ignition in a stream of carbon monoxide.

The compound Fe_3P_4 is a bluish-grey powder formed by heating ferrous chloride in phosphine, $3Fe_2Cl_2 + 4PH_3 =$

$Fe_3P_4 + 6HCl + 3H_2$: it burns when heated in the air, and loses phosphorus when ignited in hydrogen or carbon monoxide.

330. **Ferrous Phosphate**, $Fe_3P_2O_8$, may be prepared by mixing boiling solutions of ferrous sulphate and sodium phosphate. When first precipitated it is white, but it is gradually oxidised on exposure to air and turns blue. This blue compound is a ferroso-ferric phosphate, and is found native in monoclinic crystals constituting the mineral known as *Vivianite* or *blue iron earth:* its composition and physical properties are very variable, and depend upon the degree of oxidation of the mineral. Vivianite is occasionally met with on the surfaces and hollows of fossil bones. An **ammonio-ferrous phosphate**, $(NH_4)FePO_4$, analogous to the magnesium-ammonium-phosphate, is obtained in greenish-white crystalline laminæ by adding ammonia to recently-precipitated ferrous phosphate.

Ferric Phosphate, $FePO_4$, is a white insoluble powder obtained by adding common sodium phosphate to a nearly neutral solution of ferric chloride. Certain basic phosphates occur native, and frequently accompany iron ores, associated with calcium phosphate.

331. **Ferrous Carbonate**, $FeCO_3$, occurs naturally as spathose ore, and forms an important source of the metal. It is frequently found in rhombohedral crystals, known under the names of *chalybite*, *siderite*, or *brown spar; sphærosiderite* is a botryoïdal form of the same compound, principally met with in trap rocks. It may be obtained artificially in minute rhombohedrons by heating a solution of ferrous chloride with calcium carbonate under pressure. The **hydrated carbonate** is formed by mixing solutions of a ferrous salt and an alkaline carbonate. It is greenish-white when first prepared, but rapidly becomes dark green, and eventually red, owing to oxidation and loss of carbon dioxide. A hydrate of the composition $FeCO_3.H_2O$ has been found to occur naturally: it is permanent in the air, and is scarcely attacked by acids. Ferrous carbonate is soluble in carbonic acid solutions, and hence is frequently met with in natural waters, *e.g.*, in so-called chalybeate springs. No ferric carbonate has been obtained.

Comparatively few definite compounds of silicic acid with oxides of iron are known. *Fayalite* or *iron chrysolite* has the formula Fe_2SiO_4; *nontronite* appears to possess the formula $Fe_2O_3.3SiO_2.5H_2O$; *degreroïte* has the composition $Fe_2O_3.SiO_2 3H_2O$; and *anthosiderite* that of $2Fe_2O_3.9SiO_2.3H_2O$.

Compounds of iron impart to borax in the outer flame a brownish-yellow colour; in the inner flame the colour changes to green.

Ferrous salts usually possess a light-green or greenish-blue colour which is visible even in dilute solutions. Ammonium sulphide, added to the solutions, precipitates the hydrated black sulphide soluble in hydrochloric acid. Potash yields white ferrous hydrate which rapidly becomes green and ultimately red from absorption of oxygen. Ammonia forms a similar precipitate which is partially dissolved on adding excess of the precipitant; in presence of large quantities of ammoniacal salts the hydrate is not formed. Potassium ferrocyanide forms a white precipitate which rapidly changes to blue: potassium ferricyanide forms a dark-blue precipitate (Prussian blue). With potassium sulphocyanate no change is observed.

Ferric salts generally possess a yellow or brownish-yellow colour in solution; on heating, the colour becomes more intense. On treatment with sulphuretted hydrogen, the solutions become turbid from the precipitation of sulphur, the iron salt being simultaneously reduced to a ferrous compound:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

Ammonium sulphide forms a black sulphide. Excess of potash or ammonia yields the brown ferric hydrate. Potassium ferrocyanide forms Prussian blue. Ammonium or potassium sulphocyanate produces a blood-red colouration which is perceptible even in highly dilute solutions.

332. **Ruthenium**—Symbol Ru; atomic weight 104.—This metal occurs associated with platinum, iridium, osmium, etc.; it was discovered by Claus in 1844. It is found mainly in the portion of the ore insoluble in aqua-regia, which

consists principally of osmiridium. The residue is mixed with common salt and heated in chlorine; the mass is treated with water, and the solution mixed with ammonia, whereby a mixture of ruthenium sesquioxide and osmium dioxide is precipitated. The mixture is washed with nitric acid, and heated in order to expel the osmium as the volatile tetroxide. The residue is heated with potash, and the potassium rutheniate which is formed is dissolved in cold water: on adding nitric acid to the clear solution, the black ruthenium sesquioxide is precipitated; on ignition in hydrogen it yields the metal.* Ruthenium is one of the most infusible of metals: after fusion in the hottest portion of the oxyhydrogen its specific gravity is 11·4. It is almost insoluble in aqua-regia, but when finely divided it is readily attacked by melted potash.

Ruthenium Monoxide, RuO or Ru_2O_2, is a dull-grey powder formed on heating the dichloride in a stream of carbon dioxide.

The **sesquioxide**, Ru_2O_3, is a blue powder obtained by heating finely-powdered ruthenium in air. It may be prepared as a dark brown hydrate, $Ru_2O_3.3H_2O$, by adding an alkaline carbonate to a solution of ruthenium trichloride.

The **dioxide**, RuO_2 or Ru_2O_4, is formed by roasting the disulphide, or by strongly heating ruthenic sulphate. On adding caustic soda to a solution of the sulphate, the hydrated dioxide, $RuO_2.2H_2O$, is precipitated; it is soluble in acids, and in excess of the alkali.

The **trioxide** or **ruthenic acid**, RuO_3, is obtained in combination with potassium by fusing any of the preceding compounds or the metal, with potassium hydrate. Potassium rutheniate is soluble in water, forming an orange-coloured liquid.

The **tetroxide**, RuO_4 or Ru_2O_8, is a golden-yellow crystalline powder, formed by heating a mixture of ruthenium, caustic potash, and nitre, dissolving the mass in water, and treating it with chlorine. Great heat is evolved, and the tetroxide sublimes in crystals which melt at 58°: at 108° it decomposes with explosive violence, forming the metal, free oxygen and ozone. It is slightly soluble in water, and its solution is rapidly decomposed on exposure to light.

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* For further particulars respecting the separation of the platinum metals on the large scale, see Hofmann's "*Bericht über die Entwickelung der Chemischen Industrie.*"

333. **Ruthenium Dichloride**, $RuCl_2$ or Ru_2Cl_4, exists in two modifications, one of which is soluble, the other totally insoluble in water and in acids. The insoluble modification is a black crystalline powder, formed by heating the metal in chlorine. The soluble dichloride is obtained by passing sulphuretted hydrogen into a solution of the trichloride. The yellowish-brown disulphide, RuS_2, is precipitated, and the liquid acquires a blue colour—

$$2Ru_2Cl_6 + 4H_2S = 2RuS_2 + Ru_2Cl_4 + 8HCl.$$

The **trichloride**, Ru_2Cl_6, is a yellowish-brown, deliquescent, volatile substance, obtained by adding an acid to solution of potassium rutheniate, and redissolving the precipitate of hydrated sesquioxide in hydrochloric acid. When heated, it decomposes into hydrochloric acid and the sesquioxide. It forms double salts with the alkaline chlorides which are sparingly soluble in water, and readily decomposed on heating.

The **tetrachloride** exists only in union with alkaline chlorides, forming salts analogous to the corresponding compounds of platinum. On boiling the **ammonium chlororutheniate**, $(NH_4)_2RuCl_6$, with ammonia, and concentrating the solution, bright-yellow crystals of the **tetra-ammoniohyporuthenious chloride**, $[N_2H_4Ru(NH_4)_2]Cl_2.3H_2O$, are deposited. On boiling this compound with silver oxide, the corresponding oxide, $4NH_3.RuO$, is formed: it decomposes on heating, forming the **diammonium oxide**, $2NH_3.RuO$ or $(N_2H_6Ru)O$, which yields yellow-coloured salts which are perfectly stable.

Ruthenium or its compounds, fused with nitre on platinum-foil, yield potassium rutheniate, which on treatment with water forms a reddish-yellow solution; on the addition of a few drops of nitric acid the black sesquioxide is produced; on gently warming this precipitate with hydrochloric acid it dissolves, forming the trichloride, and on treating the solution with sulphuretted hydrogen, and filtering from the precipitated sulphide, a deep-blue solution of the dichloride is formed.

Ammonium sulphide added to solutions of ruthenium salts precipitates the brownish-black sulphide. Potassium sulphocyanate gives a deep purple-red colouration, changing to violet on heating. Lead acetate produces a dark-reddish-purple precipitate. Mercuric cyanide forms a blue precipitate. The alkaline nitrites form precipitates of double salts, soluble in excess of the precipitant; on adding a few drops of ammonium sulphide to the solution, it acquires a deep-red colour, which gradually changes to brown.

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334. Osmium—Symbol Os; atomic weight 199·1.—This metal was discovered by Tennant in 1803: it is always found associated with platinum and iridium, and is contained in the residue left on treating the ore with nitrohydrochloric acid. When osmiridium is heated in air or in oxygen, the osmium is volatilised as the tetroxide. To obtain the metal the osmic tetroxide is digested with mercury and hydrochloric acid; the oxide is thus reduced, and the metal amalgamates with the mercury. On distilling the amalgam in hydrogen the osmium is left in the spongy state; or the osmic tetroxide is heated with finely-divided carbon in a current of nitrogen; or it is converted into the ammonium salt which is then decomposed by sulphuretted hydrogen, and the osmium sulphide is strongly heated in a gas-coke crucible until the sulphur is expelled. Osmium appears to be the most infusible of the metals; it is much harder than glass, and crystallises in cubes or rhombohedrons resembling cubes. It has a greyish-blue colour inclining to violet. Its density is 22·48; hence it is the heaviest body known. When finely divided it burns on being heated in the air, forming the volatile tetroxide.

335. Osmium Monoxide, OsO or Os_2O_2, is obtained by igniting osmous sulphite, $Os_2(SO_3)_2$, formed by mixing solutions of sulphurous acid and osmium tetroxide; it is also formed as a dark-blue hydrate by adding potash to a solution of the sulphite. It dissolves in hydrochloric acid, and the solution rapidly absorbs oxygen from the air.

The **sesquioxide**, Os_2O_3, is obtained by heating potassium or ammonium chlorosmite with sodium carbonate in carbon dioxide, as a black amorphous powder. It may also be prepared in copper-red scales by heating osmium with osmic tetroxide.

The **dioxide**, OsO_2 or Os_2O_4, is formed by heating a mixture of potassium chlorosmate and sodium carbonate in carbon dioxide. If a solution of the chlorosmate be boiled with potash solution **osmic hydrate**, $Os_2(OH)_8$, is formed. On heating this compound it is decomposed into the dioxide, tetroxide, and free hydrogen: $2Os_2(OH)_8 = Os_2O_8 + Os_2O_4 + 4H_2 + 4H_2O$.

The **trioxide**, OsO_3, is known only in combination in the so-called **osmites**, salts obtained by reducing an alkaline solution of the tetroxide. The potassium compound $OsK_2O_4.H_2O$ may be obtained in large red octohedral crystals by mixing solutions of potassium osmate and potassium nitrite.

The **tetroxide**, or **osmic acid**, OsO_4, is formed by heating the metal or any of the lower oxides in oxygen gas, or by heating the oxides with nitric acid. It is a fusible volatile substance, possessing an intensely pungent and irritating odour (whence the name of the element, from *οσμη*, odour). It has a strong acrid taste, and is very poisonous. It is soluble in water, and is an energetic oxidising agent, bleaching indigo, and oxidising alcohol to aldehyd and acetic acid, and liberating iodine from potassium iodide. The oxide has no acid properties; on adding it to solutions of the alkalies no salts are formed: the osmic acid is partially volatilised on evaporating the liquids.

336. Osmium Dichloride, $OsCl_2$ or Os_2Cl_4, is obtained as a dark-blue sublimate by heating the metal in dry chlorine gas. It dissolves in water with a violet-blue colour, and its solution rapidly absorbs oxygen.

The **trichloride**, $OsCl_3$ or Os_2Cl_6, is also formed by the regulated action of chlorine on the metal. It is very unstable; its solution rapidly absorbs oxygen from the air, and is eventually decomposed into a mixture of oxides of osmium and free hydrochloric acid. It forms a more stable compound with potassium or ammonium chloride. **Potassium chlorosmite**, $K_3OsCl_6 3H_2O$, forms reddish-brown crystals, soluble in water, with a deep cherry-red colour. The salt is decomposed on heating.

The **tetrachloride**, $OsCl_4$ or Os_2Cl_8, is formed by the continued action of chlorine on the metal. It is very unstable, and on solution is gradually decomposed into osmic oxide and hydrochloric acid. This chloride unites with the alkaline chlorides, forming readily decomposable salts, termed **chlorosmates,** of the general form M_2OsCl_6.

On heating an ammoniacal solution of the tetroxide, a basic compound of the composition $N_2H_6OsO_2.H_2O$ is obtained. It forms salts with acids. But little is known respecting the ammoniacal osmium bases.

Osmium or its compounds, when heated with nitric acid, form the tetroxide, which is readily recognised by its remarkable smell. This constitutes the most characteristic test for the element.

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QUESTIONS AND EXERCISES.

CHAPTER I.

1. Define the terms *atom* and *molecule.*

2. What is meant by *chemical affinity?* Give illustrations of the modifying influence of external circumstances on the mutual affinities of bodies.

3. Give some account of the relations of chemical affinity to heat.

4. What is meant by the specific volume of a body? Give an account of what is known concerning the specific volumes of liquids and solids.

5. Explain what is meant by quantivalence, and point out its classificatory value.

6. Give an account of Mendelejeff's laws of periodicity.

CHAPTER II.

7. Explain the construction of the spectroscope.

8. What is the origin of the Fraunhofer lines?

9. What is an absorption spectrum?

10. What is meant by the term *electrolysis?* Explain the action of the electric current on water and solutions of hydrochloric acid, common salt, sulphuric acid, and copper sulphate.

CHAPTER III.

11. What is a crystal? How many crystallographic systems are there, and how are they distinguished?

12. What is a hemihedral form? What are twin-crystals?

CHAPTER IV.

13. How many metals are there?

14. Which is the heaviest metal? Which is the lightest?

15. Give the freezing and boiling points of mercury, zinc and cadmium.

16. What is an alloy?

17. State the various modes of preparing the metallic oxides, and describe their general properties.

18. How are the hydroxides usually obtained, and what are their general properties?

19. Give a general account of the modes of obtaining the haloid combinations of the metals.

20. Give an account of the general properties of the metallic sulphides, sulphites, and sulphates.

21. How are the nitrates and nitrites of the metals obtained, and what are their chief properties?

22. Describe the general modes of preparing the phosphides, hypophosphites, phosphites, and phosphates of the metals.

23. Give a general account of the modes of obtaining the metallic carbonates, silicates, and describe their leading properties.

CHAPTER V.

24. Give the names of the members of the monad group of metals, and point out their analogies and dissimilarities.

25. Give an account of lithium and its compounds.

26. What are the chief naturally-occurring sodium compounds? How is the metal obtained, and what are its properties?

27. How is caustic soda prepared on the large scale?

28. Describe the various modes of obtaining common salt.

29. Describe the methods of preparation and principal properties of the various combinations of sodium with sulphuric acid.

30. Give an account of the chief properties of the various sodium phosphates.

31. Give the graphic formula for microcosmic salt.

32. What is barilla, and how was it obtained?

33. Describe fully Leblanc's process for the manufacture of sodium carbonate.

34. How many tons of salt, and of sulphuric acid containing 70 per cent. of real acid, are required to make 200 tons of salt cake? Assuming that the manufacturer condenses only 90 per cent. of the hydrochloric acid evolved, how much is allowed to escape?

35. What is the composition of soda waste? How may the sulphur be recovered from it?

36. How many tons of soda crystals can be obtained theoretically from 200 tons of common salt?

37. How is bicarbonate of soda made? What is trona?

38. Describe the mode of making water-glass, and give an account of its principal applications.

39. How are sodium compounds recognised?

40. What are the principal naturally-occurring compounds of potassium?

41. How was the metal potassium obtained by Davy? Describe Gay-Lussac and Thenard's process of preparing it from caustic potash.

42. Describe the present mode of preparing potassium, and give its principal properties.

43. How is caustic potash usually prepared? What is the action of a strong solution of caustic potash on calcium carbonate?

44. What are the impurities commonly present in ordinary caustic potash? How may pure potassium hydrate be obtained?

45. What is sylvine? How is potassium iodide prepared?

46. What is the composition of plate sulphate of potash?

47. Describe the various modes of procuring pure nitre.

48. How is gunpowder made? Into what substances is it resolved on being fired?

49. Describe the mode of obtaining pearl ash.

50. How are potassium compounds recognised?

51. Give an account of the compounds of cæsium and rubidium.

52. What is the nature of the so-called ammonium-amalgam?

53. What is the action of sulphur trioxide and carbon dioxide upon (1) dry ammonia, and (2) upon ammonia in aqueous solution?

54. What is formed by the action of phosgene gas on dry ammonia?

55. Give an account of the different ammonium carbonates.

56. How does silver occur in nature? Describe the various modes of obtaining it from its ores.

57. How is *lunar caustic* made?

58. What is the composition of the body formed by dissolving silver chloride in solution of sodium thiosulphate?

59. Give the chief tests for silver.

60. Give an account of thallium and its compounds, with special reference to the points of analogy with and difference from potassium and its compounds.

CHAPTER VI.

61. Enumerate the members of the dyad group of metals.

62. Why is beryllium regarded as allied to magnesium and zinc?

63. Give the general properties of the metals of the alkaline earths, and their principal compounds.

64. How is magnesium obtained? What is formed when it burns in the air?

65. Give the composition of the following substances—carnallite, epsomite, kieserite, astracanite, and polyhalite.

66. What is the composition of the fusible calculus?

67. Describe the various modes of obtaining magnesium carbonate from dolomite. What is the composition of *magnesia alba?*

68. Give the chemical formulæ of the following minerals—olivin, augite, serpentine, meerschaum, steatite, and talc.

69. How may compounds of magnesium be recognised?

70. Name the principal naturally-occurring compounds of calcium.

71. How is lime obtained on the large scale? State its chief uses.

72. How does hydraulic mortar differ from ordinary mortar?

73. What is the formula of the salt having the following percentage composition?

Calcium,	38·72
Phosphorus,	20·00
Oxygen,	41·28
	100·00

74. Explain the formation of stalactites and stalagmites.

75. Give the graphic formulæ for tabular-spar and diopside.

76. Give the tests for calcium compounds.

77. Give an account of the compounds of barium and strontium, indicating their chief points of difference.

78. Explain the action of oxygen on barium monoxide, and show how by means of this action oxygen can be obtained from the air.

79. What is the origin of the word copper? How does this body occur in nature?

80. Describe the general mode of obtaining copper from its ores.

81. How is copper obtained from burnt pyrites?

82. Give the chemical formulæ of the following minerals—melaconite, atacamite, antimonial copper, chalcopyrite, malachite, azurite, dioptase, and chrysocolla.

83. What is phosphor-bronze?

84. Give the chief tests for copper.

85. What are the principal ores of zinc? Describe the various modes of obtaining the metal.

86. What are the impurities usually met with in spelter? Give the properties of the pure metal.

87. What is the composition of the following alloys—brass, Muntz metal, pinchbeck, and tombac?

88. Give the chemical formula and percentage composition of zinc white.

89. Give the composition of siliceous calamine, and state the peculiarity of its crystalline form.

90. How may compounds of zinc be recognised?

91. Give an account of cadmium and its compounds

92. Write a short history of palladium and its compounds.

93. Name the chief ores of mercury, and describe the mode of extracting the metal.

94. Describe the action of chlorine upon mercuric oxide.

95. How is calomel obtained? What is the action of ammonia upon it?

96. Describe the mode of preparing corrosive sublimate.

97. How would you distinguish between the two chlorides of mercury?

98. What is the composition of vermillion, and how is this body prepared?

99. Give the composition of the *white precipitates* of mercury.

100. What is Nessler's fluid, and how is it prepared?

CHAPTER VII.

101. Specify the members of the triad group of the metals.

102. Give some account of gallium and its compounds.

103. Why is indium regarded as a member of the triad group?

104. Describe the mode of obtaining antimony.

105. How is stibine obtained? What is the action of heat upon it?

106. What is the composition of tartar emetic? How is it obtained?

107. Give the composition of the following substances—antimony ochre, butter of antimony, powder of Algaroth, senarmontite, valentinite, stibnite, boulangerite, and Schlippe's salt.

108. How may antimony be distinguished from arsenic?

109. Describe the mode of obtaining bismuth.

110. Explain the action of water upon bismuth trichloride.

111. Give some account of the compounds of yttrium, erbium, and didymium, with special reference to their spectroscopic characters.

112. How does indium occur in nature? How may it be recognised?

113. What are the principal sources of gold? Describe the mode of extracting and purifying it, and state its chief properties.

114. What is the composition of standard gold? How is the fineness of gold estimated?

CHAPTER VIII.

115. Give the names of the members of the tetrad group.

116. Give the graphic formulæ for potash-alum, spinel, and kaolin.

117. What is the principal ore of tin? Where does it mainly occur, and how is the metal extracted from it?

118. Describe the leading properties of tin, and give the composition of its chief alloys.

119. How is tin-plate made?

120. How is stannate of soda prepared?

121. Give the composition and mode of preparation of the following compounds of tin—cassiterite, butter of tin, "pink-salt," "tin-salt," and mosaic gold.

122. What is the purple of Cassius, and how is it prepared?

123. How is aluminium prepared? Give its chief properties.

124. Describe the various forms of alumina and its hydrates.

125. What is a lake? Describe the action of a mordant.

126. How is alum made?

127. Give the composition of the following minerals:—wavellite, torquoise, staurolite, alum-stone, cryolite, and emery.

128. Describe briefly the manufacture of earthenware.

129. How may porcelain be distinguished from earthenware?

130. State the principal varieties of glass, and describe the mode of their manufacture.

131. How is toughened or tempered glass made?

132. Give the composition of ultramarine, and state how it is prepared?

133. Specify the principal sources of titanium.

134. What is the action of chlorine upon a heated mixture of rutile and charcoal? Describe the properties of the product thus obtained.

135. Name the chief sources of cobalt. What is the composition of the following compounds of cobalt—zaffre, smalt, Thénard's blue, Rinman's green, and cobalt yellow?

136. What is the action of a solution of cobalt nitrate or chloride upon a solution of bleaching powder?

137. How may compounds of cobalt be recognised?

138. How is nickel obtained? To what use is it applied?

139. How may nickel be distinguished from cobalt?

140. Where is platinum chiefly found, and how is it extracted?

141. What is platinum-black? What is its action upon a mixture of oxygen and hydrogen?

142. Why is it possible to fasten a wire of platinum and not one of iron or copper into a glass vessel by fusion?

143. What is the composition of iridosmine? How is iridium obtained from it?

144. What are the chief sources of lead? Describe the mode of obtaining it from its ores.

145. Describe the desilverising processes of Pattinson and Parkes.

146. Describe the English and German methods of cupellation.

147. Give the composition of the following alloys of lead—type-metal, solder, pewter, Queen's metal.

148. Describe the manufacture of litharge and red lead.

149. What is the action of (1) nitric acid (2) hydrochloric acid, and (3) acetic acid upon red-lead?

150. What is formed on boiling a solution of manganous sulphate with nitric acid and lead dioxide?

151. Give the composition of the following oxychlorides of lead: matlockite, mendipite, Turner's yellow, and Cassel yellow.

152. State the composition and crystalline form of galena. What is the action of (1) dilute nitric acid, and (2) strong nitric acid upon it?

153. Give the chemical formulæ of the following minerals: pyromorphite, anglesite, lanarkite, cerussite, and lead ochre.

154. Describe the mode of manufacturing white lead by the Dutch process.

155. Give the chief tests for lead.

CHAPTER IX.

156. Name the members of the pentad group of the metals.

157. Point out the relations of vanadium to phosphorus.

158. Give an account of vanadium and its compounds.

CHAPTER X.

159. Give the names of the members of the hexad group of metals.

160. Give the composition and graphic formulæ of chromyl chloride, dipotassium dichromate, chrome iron-ore, hausmannite, braunite, psilomelane, and dipotassium permanganate.

161. What are the chief compounds of molybdenum?

162. What is the nature of the precipitate obtained on adding ammonium molybdate solution to a dilute solution of a phosphoric acid?

163. State the chief sources of tungsten.

164. Describe the various chlorides of tungsten.

165. How is the metal uranium obtained?

166. Name the principal naturally-occurring compounds of uranium.

167. How is potassium bichromate made from chrome iron-ore?

168. Give the composition of the following substances—chrome green, chrome yellow, chrome red, crocoisite, and chrome alum.

169. How is chromyl dichloride obtained? What is formed on heating it to a high temperature in a sealed tube?

170. Give an account of the various oxides of manganese, and explain the action of heat upon each.

171. Describe Weldon's process for the recovery of manganese from the "still-liquor" obtained in the manufacture of chlorine.

172. How is potassium permanganate prepared?

173. Describe the general nature of meteoric iron.

174. Name the principal ores of iron, and point out their chief peculiarities.

175. Describe the general method of analysing an iron-ore.

176. Give an account of the manufacture of cast-iron.

177. Describe the chief varieties of cast-iron.

178. What causes the peculiar smell noticed on dissolving cast-iron in dilute hydrochloric or sulphuric acid?

179. What is the general composition of spiegel-eisen?

180. How does wrought-iron differ from cast-iron?

181. Describe the operation of puddling, and explain the chemical nature of the process.

182. How is merchant iron produced from puddled bar?

183. What is the influence of silicon, phosphorus, and sulphur, on iron?

184. Describe the Catalan forge.

185. What is steel? How does it differ from wrought-iron?

186. Describe the cementation process of making steel, and explain the theory of the method.

187. How is cast-steel made?

188. Describe the Bessemer process of manufacturing steel.

189. Describe the peculiarities of the Bessemer spectrum.

190. Describe Eggertz's method of estimating the amount of carbon in iron and steel.

191. State the properties of pure iron.

192. How many oxides of iron are there, and what are their chief properties?

193. Explain the action of oxide of iron in promoting the decomposition of organic matter.

194. Explain the action of heat and light upon dilute solutions of ferric chloride.

195. Give the chemical formulæ and properties of the principal compounds of sulphur and iron.

196. How is green vitriol made? What is the action of nitrogen dioxide and trioxide upon its aqueous solution?

197. How is iron-mould produced?

198. How may ferrous salts be distinguished from ferric compounds?

199. What is the action of sulphuretted hydrogen upon a solution of ferric chloride?

200. Give an account of the chief properties of ruthenium and osmium, and of their principal compounds.

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